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I. *Some Spiral Figures observable in Crystals, illustrating the Relation of their Optic Axes.* By LEWIS WRIGHT*.

[Plate I.]

THE true relation of the optic axes in uniaxial and biaxial crystals has always been an interesting subject. We know that if the crystals be both polarized and analyzed circularly, and we disregard any dispersion of the axes for various colours, the axis of a uniaxial and *one* of the two axes of a biaxial present ultimately similar phenomena. Here, for example, is the well known system of rings and brushes presented by a plate of calcite (Pl. I. fig. 1). As is well known, if we interpose between the polarizer and the crystal a quarter-wave plate, the black cross disappears, to be replaced by grey nebulous lines (fig. 2), on alternate sides of which the quadrants are dislocated; and if now we interpose a second quarter-wave plate between the crystal and the analyzer, when the latter is either crossed or parallel even these lines disappear, and we get simply a series of circular rings with no break whatever (fig. 3). Let us now take a plate of sugar cut across one of its two optic axes. This crystal is suitable for our purpose as having scarcely any axial dispersion, so that one of its axes gives sensible circles, which many other biaxials do not.

* Read November 12, 1881.

Placing it in the stage, we have a system of rings traversed by a straight brush (fig. 4), which, on interposing the first quarter-wave plate, becomes a grey line, on each side of which the semicircles are dislocated (fig. 5); but now interposing the second quarter-wave plate, we have perfect unbroken circles as before (fig. 6).

Now this might seem to imply that the optic axis of the uniaxial calcite resembled in its character that of a *single* axis of the sugar, or biaxial. It need hardly be said here, that such was not the view taken of the matter by those intellectual giants who chiefly shaped into definite form the theory of double refraction in crystals. Gradually this theory was simplified, until Fresnel finally framed the conception of three elasticities within the crystal in the direction of three rectangular axes. If all three elasticities were equal, there was no double refraction; if only two were equal, there was a single axis of no double refraction in the direction of the third; if all were unequal, there were two such optic axes. In any conceivable case the wave-surface could be calculated or geometrically projected upon this hypothesis; and it is needless to repeat how, after its author had passed away, Sir William Hamilton worked out from his conceptions the remarkable and unforeseen results of conical and cylindrical refraction which were experimentally verified by Dr. Lloyd (also removed from us during the past year). That extraordinary verification of Fresnel's theory, which makes the optic axes mere resultants of three rectangular elasticities, has always been considered to have placed it upon an impregnable basis, and seems only to have left for future experiment the possibility of perhaps some further illustration, which is the sole object of this paper.

For observe that, according to this theory, the optic axis of our calcite would *not* correspond in character with a single axis of the sugar or any other biaxial, but must be regarded as simply a limiting case in which *both* such axes coincide. This is well illustrated by the celebrated experiments of Professor Mitscherlich in gradually applying heat to crystals, especially to a crystal of selenite, and thereby altering by the unequal expansion their respective elasticities.

Of the two axes gradually approaching till they unite into one as the elasticities are gradually equalized, there could be

no clearer proof than this old experiment. But it seemed worth while to seek further illustration of one particular point, viz. that the axis of the uniaxial crystal did actually retain or embrace within itself, in some visible form, optical characteristics of the two axes thus brought, temporarily or permanently, into coincidence. This object seemed most likely to be obtained by the aid of quartz, or some other substance possessing similar properties of rotary polarization. Such substances having, apart from their ordinary doubly-refractive effects, two different *axial* velocities or waves capable of being brought into interference, and the two axes of a biaxial being according to hypothesis dissimilar, one being principal and the other secondary to it, it seemed probable that by proper means the two axes might be made to exert some kind of differential or selective action upon the two sets of waves passing through the rotary substance. I was confirmed in this expectation by the curious double spiral, first noticed by Sir George Airy, as displayed by quartz itself when subjected to circularly polarized light, the cause of which appeared to me to be connected with this very matter, as we shall presently see to be the case. After observing with more care than usual, therefore, the effects of quartz in combination with other crystals in various ways, most of which have been described by various observers, I finally adopted the following arrangement:—We introduce first, next to the polarizer, a quarter-wave plate, then (in the convergent rays) a plate of calcite, and next to this a plate of quartz 5 to $7\frac{1}{2}$ millim. thick. The result of this arrangement is the system of double spirals, mutually enwrapping each other, now on the screen (fig. 7). This figure only changes in colour, or moves to or from the centre, as the analyzer is rotated—though there are of course only certain complementary positions of the polarizer, related to that of the quarter-wave plate, which produce them. The point to be here observed is the *double* character of the spiral in this uniaxial crystal.

This figure, however, so closely resembled in all but the number of its convolutions the one exhibited by quartz alone, as described by Sir George Airy in the Cambridge Transactions for 1831, that it might possibly be due to the quartz itself in the convergent light; it was necessary to see if there

were any differential results with other crystals, and, finally, to see if they remained when any such possible cause for them was removed. A single axis of sugar was therefore next placed in the crystal-stage in place of the calcite; and the result is again before you (fig. 8). Observe that, with this single axis of a biaxial, we no longer have the double spiral, but a single one, corresponding exactly to the supposed relation of which we are in search, and also showing that the figures are not proper to the quartz as such, but to some selective action of the axes of the other crystals upon the two axial waves of the quartz and their interferences. A single axis of iron sulphate, and this crystal, cut across a single axis of a topaz, gives similar single spirals.

The single axis being thus tested, we place in the stage a biaxial cut across both axes—in this case nitre (fig. 9). The supposed relation still holds good: each axis now has its own distinct spiral, and the two mutually enwrap one another as in the calcite.

The same is true of crystals whose axes include much wider angles; but to show their spirals we must alter our arrangements. Extra convergent lenses are added in a moment; but if we placed a quartz plate in the strongly convergent light we have to employ to bring both axes of such crystals upon the screen togther, the rings and spirals proper to the quartz itself, which have not appeared in the very moderate convergence so far used, would now appear so strongly as to overpower and distort those due to the crystals under examination. We also want to ascertain beyond doubt that the effects are not due to any *convergence* of the rays traversing the quartz, but solely to selective action upon the right-handed and left-handed waves traversing it axially. We therefore reverse the combination, placing a large plate of quartz about $7\frac{1}{2}$ millim. thick next to the polarizing Nicol, in the parallel rays, and removing the quarter-wave plate to a position between the crystal to be examined and the analyzer. Of course, as it is now the analyzer which is related in position to the quarter-wave plate, the spirals only appear in complementary positions; while, on the other hand, when the analyzer is in those positions the polarizer may be completely rotated. Of course, also, we might have adopted this arrangement all along; but

I have given the experiments as they were made, in order to show how each successive question was determined.

A multiplicity of crystals would be useless: three of various angles will show the uniformity and gradation of the phenomena. Our former crystal of topaz cut across one axis, being thin enough also for the more convergent arrangement, will show that the single spiral appears precisely as before, the convolutions being simply closer in this strongly convergent light. Next we will take again the small angle of another nitre crystal, cut thin enough to show conspicuous figures in the convergent apparatus (fig. 10). Observe that we can now barely distinguish its two spirals, by their oval contour, from those just now presented by the calcite: they are a little *drawn out*, as it were, precisely as we should expect; and that is all; otherwise the visible elements are manifestly the same in both. Arragonite (fig. 11), with an angle of $18\frac{1}{2}$ degrees, shows a spiral of several turns round each axis; but still they finally enwrap each other: and now mica, with an angle in this specimen of 60° or 70° (fig. 12), gives the same phenomena. With the wider separation, the spiral round each axis has room to show separately more of the character of the single axis of the sugar; but the two always preserve the same relation, and only crystals which, owing to very powerful dispersion of their axes, fail to show perfect lemniscates in the ordinary way, fail for the same reason to show these figures complete. Here, for instance, is a plate of borax, whose axial dispersion is considerable and peculiar; but as this still leaves the ordinary lemniscate curves tolerably unbroken, we can trace the spirals without difficulty.

That these figures are solely due to differential action upon the interferences of the quartz rotational colours, we shall demonstrate absolutely in a few minutes; meantime we can almost prove it in two ways. First, though all the arrangements remain complete, the spirals disappear or lose their character in monochromatic light; and, secondly, substituting a quartz of opposite rotation, the direction of the spirals is, as you see, reversed.

And now we will project the beautiful experiment of Prof. Mitscherlich, afterwards applying to it this additional method of analysis. There are the two axes arranged vertically; as

we apply heat they gradually unite. The crystal is now uniaxial. And now the axes open out again, but horizontally. It is a beautiful demonstration, which never loses its fascination for the student. We now add our arrangements for the spirals. There they are, arranged perpendicularly on the screen. They approach as the crystal is heated, till now we have them as in the calcite. Now they open out again in a horizontal direction, like those of a plate of nitre turned round 90° in its own plane. Observe that all through we have the *double* spiral. We can only get a single one by taking a single axis; while the axis of a uniaxial always preserves what we may call its "twin" character. Thus we have the ocular illustration sought at the commencement, of the precise relation predicated by Fresnel's theory between the axes of uniaxial and biaxial crystals, and that the former class do contain, within their single axis, elements (capable of being made optically visible) of both the axes in the latter class.

We have here also objectively demonstrated the reason of the double spiral, first observed by Mr. Airy, in quartz itself. We see that the quartz, considered as an ordinary uniaxial crystal, owing to its peculiar effects upon plane-polarized light passing through it axially, is able to *show its own spirals*, which of course are double. They are not seen at all in parallel light; and, on the other hand, if we increase the rings by convergence, the spirals become more definite. Here, for instance, is a rather thin quartz (one of a pair generally used to show Airy's spirals): in this strongly-convergent circularly polarized light, it shows spirals as well defined as did our calcite. A crucial test of this view readily suggests itself. If it be well founded, obviously we can combine the two properties of our quartz artificially, as it were, since many fluids possess the same power of dividing into two opposite circular waves, differently retarded, a plane-polarized ray. If therefore we take a column of such fluid of sufficient length, and any ordinary uniaxial crystal, the one will represent the peculiar axial properties, and the other the ordinary doubly-refractive properties of the quartz; and the two ought to give similar double spirals. In fact an adequate column of fluid ought to replace the quartz successfully in all the foregoing

experiments. Our last step, therefore, is to prove that this is the case. I have here a tube of oil of lemons 200 millimetres (8 inches) in length, which we introduce into the parallel-plane-polarized beam in place of the quartz, whose axial properties it now represents. In the crystal-stage we adjust the calcite, which in all except being a negative crystal (and a positive one would be just the same) represents the ordinary doubly-refractive properties. And now introducing the quarter-wave plate between crystal and analyzer, we have the spirals as given by the quartz in all respects. The same effects are produced by other crystals, any slight inferiority being due to the slightly yellowish tint of the fluid, which so far approximates to homogeneous light. Spirit of turpentine is free from this defect; but we could hardly project through a tube of sufficient length.

These phenomena hold good through all the ordinary analogies with, or substitutes for, natural crystals. This round disk of chilled glass, placed in parallel light, which behaves in all other respects like a crystal in convergent light, also gives double spirals like those of the calcite. I have here also an artificial uniaxial crystal formed of crossed mica-films, after Norremberg, and an artificial quartz of mica-films, after Reusch, for both of which I am indebted to my kind friend Mr. Fox, who made them with his own hands. The first gives the calcite spirals with a quarter-wave plate and quartz; the Reusch preparation gives the quartz spirals with the quarter-wave plate alone.

These experiments of course add nothing to the theory of the matter, and make no such pretension; their whole interest lies in the visible, ocular demonstration they afford of the truth of conclusions long ago worked out by the brilliant mathematical genius of Fresnel. But to the best of my belief they are new; and if it should prove that some other student has been before me, I hope the beauty of the phenomena may excuse my bringing them before you.

II. *On Integrating and other Apparatus for the Measurement of Mechanical and Electrical Forces.* *By* C. Vernon Boys, *A.R.S.M., Demonstrator of Physics in the Normal School of Science, South Kensington*.*

[Plates II., III.]

When in February of this year I described my first integrating-machine† before the Physical Society, I felt that, unless the tangent principle could be so applied as to admit of an indefinite growth of the integral, such principle would be useless for practical purposes. In that machine the integral is determined by the *position* of a cart, and so is limited by the size of the apparatus. Since that time I have devised a variety of methods of applying the tangent principle in which the integral is determined by rotation, and so there is no limit to the extent to which the integral may grow. In the following paper, which is divided into two parts, I have given in the first a description of a variety of integrating-machines, while in the second are some useful applications of the most simple form of integrator described in Part I.

Part I.

At the present time there seem to be three types of integrating-machines: 1st, those that may be called radius machines, comprising Sang's planimeter, Clerk Maxwell's sphere machine, and Sir James Thomson's disk sphere and cylinder integrator (Ashton and Storey's steam-power meter also comes under this head); 2nd, sine or cosine machines, comprising Amsler's planimeter and mechanical integrator, and the various wind integrators; 3rd, tangent machines, which, so far as I am aware, are represented only by the cart machine already referred to and those that are the subject of this paper. This class of machines depends on the formula for integration, which, in its geometrical application, finds a curve of which the steepness or the tangent of the inclination (i. e. $\frac{dy}{dx}$) is equal to the ordinate of the given curve or to the given func-

* Read November 26, 1881.

† Proceedings of the Physical Society, vol. iv. p. 199.

tion. In my former machine a pointer is made to follow a curve, and by so doing causes a rod to be inclined in such a manner that its tangent is equal to the ordinate. There is also a three-wheeled cart; and the plane of its steering-wheel is by simple mechanism kept parallel to this rod; moreover the horizontal component of the cart's motion is equal to that of the pointer. Under these conditions the vertical component of the motion of the cart (or, shortly, its ascent) determines the integral.

I will now show how this principle is applied in a series of machines in which the integral is determined by rotation and not by linear motion, and in which, therefore, the integral may grow indefinitely. At first let us suppose that the cart in my first machine is incapable of vertical motion; then it, in its attempt to move up or down, will push the paper in the opposite direction. If now the paper is wound on a cylinder with its axis beneath the path described by the front wheel of the cart, and if the hind wheels are supported by some other means, then the cylinder will rotate; and the rate of its rotation will be proportional to the ordinate of the given curve, and the amount of its rotation will be the integral required. Now it will at once appear that the cart and the parallel motion are not wanted, and that the inclination of what was the front wheel of the cart, and what may now be called the tangent-wheel, may be determined mechanically by the same method that was adopted to give inclination to the rod. Also if, instead of moving the tangent-wheel along the surface of the cylinder, the cylinder be moved longitudinally under the tangent-wheel while its inclination is determined by suitable means, then, as before, the rotation of the cylinder is a measure of the integral.

As the cylinder must necessarily have a finite length, it cannot be caused to move continuously in one direction under the tangent-wheel, but must be made to reciprocate. This motion is most readily produced by use of a "mangle-motion," which converts uniform circular into uniform reciprocating motion. Now, when the motion of the cylinder is reversed, so also is the direction of its rotation; and therefore either the action of the tangent-wheel on the cylinder must be reversed, or there must be a reversing-gear between the cylinder

and the mechanism employed to count its revolutions. The action of the tangent-wheel on the cylinder is most easily reversed by having two of them mounted in a frame so that they lie in the same plane, but that one is on one side of the cylinder and the other is on the opposite side. The cylinder is made to bear against one during its forward stroke, and against the other during its return stroke—a change readily effected by the mangle-motion. Then the rotation of the cylinder is independent of the direction of its longitudinal motion. When it is preferred to use only one tangent-wheel, the reversal between the cylinder and the counting mechanism can be easily and perfectly produced by using three bevel wheels and a friction-clutch actuated by the mangle-motion or even by the change of motion of the cylinder.

If the cylinder could be made long enough and the ends bent round so as to join one another, then continuous revolution of the whole ring would take the place of the reciprocation of the cylinder, and the integral would be determined by the rotation of the ring round its circular axis. Such a "smoke-ring" can scarcely be made; but an equivalent can be produced without difficulty. Let there be four barrels, each with a concave instead of a convex outline, mounted on a wheel with their axes in one plane, and with some one generating line on each a quadrant of a common circle concentric with the axis of the wheel. Also let the four barrels be geared to one another by bevel wheels (fig. 1, Plate II.). Now let a tangent-wheel be placed inside the common circle so as to touch it at its lowest point; then, if the tangent-wheel lies in the same plane as the circle, revolution of the wheel supporting the barrels will produce no rotation of those barrels; but if the tangent-wheel is inclined at all, the rotation of the barrels will be directly proportional to the tangent of its inclination, and inversely proportional to the radius of the barrel at the point of contact. This periodical inequality, due to the changing radius of the barrel, may be eliminated by using a second mechanical smoke-ring made of a series of convex barrels mounted on a wheel, with some one generating line of each a portion of a common circle which lies outside instead of inside the barrels. In this, which may be called an outside ring, the other being an inside ring, the barrels must not

be geared together. Fig. 2 is a plan on a larger scale, partly in section, showing how such barrels might be supported. Now, if this outside ring is placed horizontally within the inside ring and touching it at one point, then revolution without rotation of the inside ring will cause rotation without revolution of the outside ring; if, however, in consequence of the inclination of the tangent-wheel, the barrels of the inside ring are caused to rotate, then such rotation will cause revolution of the outside ring; and this revolution will be a true measure of the integral, as the outside ring and the tangent wheel touch barrels of the inside ring at points having the same radius. The astronomical convention with respect to the terms revolution and rotation has been used. By revolution of the ring is meant a turning of the whole round a centre; and by rotation a turning of barrels round their own axes.

Instead of a disk, a sphere similarly mounted may be used for a tangent-wheel, with the same result. Of course the cylinder will be in contact with the sphere at a point on its equator; but if the support of this globe is varied in position, so that the cylinder touches the sphere nearer the poles, then the rate of rotation will depend not only on any former inclination of the plane of the equator of the globe to the axis of the cylinder, but will also be inversely proportional to the cosine of the latitude of the point of contact. The latitude should be brought back to its original value before the rotation of the cylinder is measured. Fig. 3 shows the cylinder in contact with the sphere at a latitude λ. It so happens that the radius in the sphere at the point of contact is equal to $\cos \lambda \times$ the radius of the sphere; but this is not the cause of the introduction of that function, as the rotation of the cylinder is independent of the radius of the tangent-wheel. The true reason can be readily discovered by a simple geometrical construction, which, from the length of this paper, I omit. However, a good illustration may be seen by taking a bicycle and causing it to lean over on its side; then a given twist of the handles will be found to produce a greater deviation in the direction of its motion than would be the case if the bicycle were upright. The effect just described is most easily produced by mounting the cylinder on a rocking-frame, so that it can roll round the ball. Though the axis marked A in the

figure remains vertical, yet the effect may be considered as due to a leaning to one side of this axis. If, however, the axis A is caused to lean forwards or backwards, then the rotation of the cylinder, which is still proportional to the tangent of any rotation about A, is also proportional to the sine of the inclination of A above the horizon; so that if A is horizontal, no rotation about A as an axis will produce any effect; but as A rises higher, increased rotation of the cylinder will be produced, the maximum being when A is vertical. As in the former case, so here, the inclination of A should be brought back to its original value before the rotation of the cylinder is measured. This is the method of steering a wheelbarrow when pushing it. The elevation of the handles corresponds to the inclination of A with the horizon; the equality of the elevation of the two handles corresponds to absence of rotation about A; therefore the barrow goes straight. When turning a corner the outer handle is elevated more than the inner one; this corresponds to rotation about A; and the tangent of this rotation, multiplied by the sine of the elevation of the handles, measures the deviation of the barrow from its straight course. This deviation, then, is greater as the elevation of the handles is greater, and therefore in going round a sharp corner the handles should be raised as much as possible. By the means above described, either the quotient or the product of two functions may be directly integrated.

As in my former integrating-machine, so with these, the reciprocal of a function may be integrated by first inclining the tangent-wheel through a right angle; then, when a function passes through 0 from + to −, the tangent-wheel describes on the surface of the cylinder a cusp showing a momentary infinite motion. A machine so arranged may be used to integrate, not the reciprocal, but the function itself, if, instead of moving the cylinder longitudinally, it is caused to rotate, when the longitudinal motion, or the number of reciprocations if suitable gearing is employed, will measure the integral. In a similar way the machine as first described will integrate a reciprocal.

If for any purpose, in addition to the total result, the integral up to any time is required, a diagram must be drawn. This can be effected by covering the cylinder with a layer

of black tracing-paper, and allowing a band of paper as wide as the cylinder is long to pass between the tangent-wheel and the black surface. The length of paper passed through the machine represents the integral; and the curve drawn shows its rate of growth continuously. Should it only be required to know the amount of growth during each of a series of short intervals of time, a narrow band (which is more manageable) may be used wrapped round a small wheel at the end of the cylinder, and so arranged that at the end of each double stroke of the cylinder it is caused to bear against the point of a stationary pencil; then the pencil-marks represent equal intervals of time, while the distances between them measure the average rate of growth over each interval.

I have at present supposed that the integrating surface is cylindrical; but other surfaces of revolution may be employed for particular purposes. As the rotation of the cylinder depends on the linear motion of its surface, it is clear that its rotation must be inversely proportional to its diameter. If, therefore, instead of a cylinder any other surface of revolution is taken, its rate of rotation will depend not only on the inclination of the tangent-wheel, but also on the radius of contact. The simplest case is that of a disk with the tangent-wheel mounted so as to be capable of radial movement. Then, if the tangent-wheel moves in the direction of its own plane, it will simply describe on the disk a radial line, and there will be no rotation; but if it is inclined at any given angle the disk will rotate, and the rate of its rotation will be proportional to $\frac{1}{r}$, and its whole rotation will be $\int \frac{1}{r} dr$, which is $\log r$. Now the tangent-wheel, in its movement outwards, describes on the surface of the disk a spiral which everywhere cuts the radii at the same angle; therefore in such a spiral the angles are the logarithms of the radii; *i. e.* it is the logarithmic spiral. If the inclination of the tangent-wheel is made to depend on some function, then such double-disk machine would integrate $\frac{\phi x}{c+x} dx$, in which c is the radius of contact when $x=0$.

If the axis of the tangent-wheel is made to pass through a fixed point over the disk removed from its line of travel by a right angle, then the tangent of its inclination to the direction

of its motion is proportional to the radius of contact: but, other things being equal, the rotation of the disk is inversely as the radius of contact; therefore the amount of rotation of the disk for a given movement of the tangent-wheel is independent of the radius of contact, and the curve traced out on the disk is the spiral of Archimedes. But if, instead of passing over a disk, the tangent-wheel similarly mounted is made to pass along the surface of a cylinder, then the speed of rotation of the cylinder will be proportional to the distance of the disk from its neutral position, and its whole rotation will be $\int cx\,dx$, or $\frac{c}{2}x^2$, and the curve described on the cylinder will be a parabola. This arrangement of the disk and cylinder may be used, as described on page 16, in a polar planimeter to illustrate the formula $\iint r\,dr\,d\theta$.

After the cylinder and disk, the most simple form for an integrating surface is that of a sphere. Let a sphere be supported, with its axis horizontal, on a frame which can be made to reciprocate about a vertical axis which would, if continued, pass through the centre of the sphere; then, if a tangent-wheel is fixed so as to lie, when its inclination is nothing, in the horizontal plane which passes through the axis of the sphere, angular reciprocation, which must be less than 180°, will cause the tangent-wheel to describe on the sphere a meridian when it is in its neutral position, or a rhumb line if inclined at a constant angle. As the speed of rotation of the sphere is inversely proportional to the radius of contact—that is, to the cosine of the latitude of the point of contact—some means must be adopted whereby the rotation recorded is less than the rotation of the sphere in the same ratio. The most simple plan is to use Amsler's principle, and mount a small sliding and rolling wheel so as to be in contact with the sphere at the highest point on the equator (*i. e.* 90° from the tangent-wheel), but with its plane passing through the centre of the tangent-wheel; then the rotation of the Amsler wheel is always less than the rotation of the sphere, in the same ratio that the rotation of the sphere is too great. Instead of an Amsler wheel, a cylinder capable of moving longitudinally on its horizontal axis, and in contact with the sphere at a point exactly opposite to the tangent-wheel, would, by pure rolling

and without any sliding, take off the correct proportion of motion, since it and the tangent-wheel always touch the sphere at points having the same radius.

Fig. 4 is a perspective view of a polar planimeter in which the integration is effected by a disk sphere and Amsler wheel, as described. All the parts marked *a* belong to a rigid frame, which balances on and can turn about a vertical spindle, the top of which is just visible below the tangent-wheel *t*. The vertical spindle is fastened to the stationary wheel *w*, which rests on three feet. The segmental wheel W in gear with *w* is secured to a vertical spindle, the upper end of which carries the crutch C. Screws in the crutch form the horizontal axis about which the sphere S may rotate. The tangent-wheel *t* is mounted in a frame which can be turned about a horizontal axis *e* by means of a lever *l*. The Amsler wheel rests by its weight on the highest point of the equator of the sphere, which is shown dotted. D D is an L-shaped piece, which carries at the angle the pointer P. At the end of the long limb is a slot embracing a pin, as shown. A part of the short limb is made cylindrical; against this part rests the edge of the lever *l*. This edge is not truly radial, but is laterally displaced from the radial position to an extent equal to the radius of the cylindrical part of D D. This causes the true radius, which is parallel to the axis of the tangent-wheel, to intersect the axis of the cylinder. Now, if the pointer P is moved radially in the slot prepared for it, it is clear that the tangent of the inclination of the tangent-wheel *t* will be proportional to the square of the distance of P from the vertical axis about which the machine can turn, also that, during any turning of the machine about this axis, the sphere will turn about its vertical axis at a proportionate speed. Now it has been shown that, when the sphere is made to turn about its vertical axis, the rate of rotation of the Amsler wheel is proportional to such rotation multiplied by the tangent of the inclination of the tangent-wheel—that is, in this case to $r^2\,d\theta$. Therefore the whole rotation of the Amsler wheel is a measure of $\int r^2\,d\theta$; and so, if the pointer P is taken round any closed curve, the area of that curve may be read off from the Amsler wheel. The wheel W is three times the radius of *w*; so that the pointer may, if necessary, be taken completely round the

pole, and yet the tangent-wheel will only move 120° on the sphere in latitude. The diameter of the Amsler wheel is one third of that of the sphere, so as to restore the diminished speed. Unlike Amsler's planimeter, this one shows the increment of area for each part of a closed curve, the reason being that it is an exact mechanical equivalent of the polar formula for integration. Though the machine works very well, it cannot be compared to Amsler's as a practically convenient instrument.

An exact mechanical equivalent of the formula $\iint r\,dr\,d\theta$ would be produced by retaining all the last machine, except the short limb of the L-shaped piece D D, and mounting on the long limb a tangent-wheel to traverse a cylinder, the rate of rotation of which for a given radial movement of the pointer would be proportional to the distance of the pointer from the pole—that is, to $r\,dr$—and the whole rotation would be $\int r\,dr$. Now, if the cylinder were by its rotation caused to change the inclination of the lever l so that the tangent of the inclination of l was proportional to the whole rotation of the cylinder then, when the pointer was taken round a curve, the rotation of the Amsler wheel would be $\iint r\,dr\,d\theta$. In either case, instead of an Amsler wheel, a cylinder mounted as described on the last page would give the integral.

PART II.

The practical value of the tangent principle depends on the fact, that the only operation required of the function to be integrated is that of turning more or less a spindle and tangent-wheel, which may be as light and delicate as any part of a watch, and of which the moment of inertia may be inappreciable. This is in marked contrast to what is necessary in radius machines: the friction in the common double disk or disk and cone integrator, or the inertia of the ball in Sir James Thomson's machine, would be quite sufficient to make the former useless for the integration of such delicate forces as depend on the actions of electricity, or the latter inapplicable to machinery in rapid movement. Another point about tangent machines is, that the whole process of integration is the result of pure rolling, and any doubt that may be felt as to the effect of the sliding action on the accuracy of cosine

machines is here removed. The rest of this paper describes some applications of the disk-cylinder integrator some of which are likely to be of practical value.

Engine-power Meter.

As work is motion multiplied by pressure, the work done in an engine may be found by integrating the difference of pressure on the two sides of the piston with respect to the motion of the piston. For any one stroke, this is usually done by measuring the areas of the indicator-diagrams, one taken at each end of the cylinder, and repeating, so as to get an average value. But as the work done, or the area of the diagram, is subject to variation depending on the load, pressure, and speed, only guesses can be made as to the whole amount of work that has been done by an engine during any length of time. Any machine, therefore, that will automatically find the total work done should be of value, not only to users of engine-power, but especially to experimentalists who are engaged on testing the efficiency of engines, and on other subjects where total work done should be known. It is only fair to mention that Messrs. Ashton and Story have an engine-power meter in which the integration is effected by a double-disk integrator acting on the radius principle; but it necessarily suffers from the defects common to all radius machines. The disk-and-cylinder is especially applicable to this particular case; for it is only necessary to make the cylinder reciprocate with the piston of the engine, the motion being of course reduced to a convenient amount, and to make the tangent of the inclination of the disk vary with the difference in pressure on the two sides of the piston of the engine. Then, at any moment, the cylinder will turn with a speed which is proportional to the rate at which work is being done, and the number of revolutions, as measured by a counter, will be a measure of the work done in foot-pounds or other units during any time. Figs. 5 and 6 are views of an engine-power meter, each partly in section. A, A are two boxes with flexible covers, like the corrugated plate in an aneroid barometer. They may be filled with a mixture of glycerine and water or other liquid, and connected each with one end of the cylinder of the engine. Each diaphragm will feel the pressure, but not the heat, of the

steam or gas in the cylinder. The two diaphragms are connected by the rod r; and so the effective force tending to bend the diaphragms is the difference of pressure at the two ends of the cylinder. This is the force acting on the piston of the engine. Inclination is given to the tangent-wheel t by the rod r by a pin working in a radial slot, as is better shown in fig. 7. This arrangement causes the tangent of the inclination of the tangent-wheel to be proportional to the displacement of the rod r, and so to the force acting on the piston. C is the integrating-cylinder, which is capable of sliding along, but of turning with a wire W, which may be grooved or polygonal; pinion-wire is very suitable. The integrating-cylinder is caused to reciprocate, by means of a yoke Y and lever L, in time with the piston of the engine. The stroke is reduced to a convenient amount by attaching a string from the piston-rod to a suitable part of the lever L. Now, as the rate at which the cylinder turns is proportional to the longitudinal motion of the integrating-cylinder multiplied by the tangent of the inclination of the tangent-wheel, and as this is proportional to the motion of the piston multiplied by the force urging it, *i. e.* to the work being done, the whole number of the revolutions of the cylinder will measure the whole amount of work done. If the instrument gets out of adjustment so that the tangent-wheel is not parallel to the axis of the cylinder when there is no force, then whatever error it makes in a forward stroke it will take off in the return stroke; so that no accumulating error will be produced. The diaphragms may either be made of steel or highly elastic metal, in which case they form their own springs; or a softer metal, controlled by an external spring, might be used. If a diagram is required, one may be drawn as described on page 13. But it will not be a diagram such as is drawn by an ordinary indicator, but the integral curve of such a diagram; so that force, instead of being represented by the length of an ordinate, will be represented by steepness. Instead of diaphragms as described, spring pistons or Bourdon pressure-gauge tubes might be employed to give inclination to the tangent-wheel.

Integrating Dynamometers.

The disk-cylinder integrator may be applied to measure the whole amount of work transmitted by shafting or belting. In

the case of shafting, what is called a differential coupling—that is, a contrivance which transmits any motion, but measures the force causing such motion—is employed to give inclination to the tangent-wheel. In the case of belting, any of the known dynamometers may be employed for the same purpose; while a mangle-motion driven by the revolving shaft or travelling band, causes the cylinder to reciprocate. Either of the methods given on page 10 may be employed to produce continuous growth of the integral in one direction. As the work transmitted at any moment is force multiplied by motion, and as the tangent of the inclination of the tangent-wheel is proportional to the force, while the reciprocating motion of the cylinder is proportional to the motion, the rate of revolution of the integrating cylinder will be proportional to the rate at which work is being done, and the whole number of revolutions will give the whole amount of work done. If at any time the force causing the motion should change sign and so resist it, as is the case in an engine when there is much cushioning, then the tangent-wheel will incline the other way and take off from the record a corresponding amount of work.

Electric-Current Meters.

The application of the disk-cylinder integrator to an electric-current meter is very obvious. Figs. 8 and 9 are two views of an electric meter, in which the inclination of the magnet M is effected by the electric current passing in a large coil surrounding the instrument. The magnet M and the tangent-wheel *t* are each fixed on the same spindle, which is vertical, and which is very light and delicate. The weight of the magnet produces the necessary pressure between the tangent-wheel and the integrating-cylinder C; and as the surface of each is convex, the friction resisting the turning of the tangent-wheel by the magnet is very small. The cylinder is supported in a bell-crank frame F, which can be made to reciprocate along the wire W by means of the mangle-motion *m m*. The mangle-motion is actuated by clockwork, which may be wound by the current itself when necessary, should such a course be desirable. Fig. 10 shows the construction of a suitable mangle-motion. The pinion can turn, but not move otherwise, while the frame carrying the racks can move either longi-

tudinally or laterally. A pin projecting centrally from the pinion enters the slot, which is shaded in the figure, and so causes the pinion to gear with the two racks alternately. This lateral movement of the rack-frame is made use of to depress the integrating-cylinder during its back stroke, at which time the magnet rests on the shoulder S. As the tangent of the inclination of the tangent-wheel is proportional to the current-strength, and as the rate of rotation of the cylinder is proportional to the tangent of the inclination of the tangent-wheel, the cylinder will turn with a speed which is proportional to the current-strength, and the whole number of turns, as shown by the counter, will be a measure of the quantity of electricity that has passed. In the arrangement described, time is divided into a great number of equal intervals, and the current-strength during each alternate one considered. After any considerable time, such a sampling of the current would give just as exact a result as would be obtained by integrating continuously. A quick-return mangle-motion might be employed to diminish the proportion of ineffective time; or the whole time could be made effective by keeping the cylinder in continuous contact, and actuating a reversing-gear between the cylinder and a counter by means of the lateral movement of the mangle-motion. It would be well to employ a catch on the armature of a subsidiary electromagnet, so as to stop the clockwork, except when a current is passing. This current-meter, like Edison's electrolytic meter, is a direction-meter. If the current is passing in one direction, it counts it positive; if in the opposite direction, it counts it negative. A reverser actuated by a polarized armature could be employed to make the meter count as positive, a current passing either way, and so make it applicable to the case of alternating currents. Another kind of current-meter, which is by its nature independent of the direction of the current, would be preferable to the magnetic-needle meter and reverser combined.

Figs. 11 and 12 represent an electric-energy meter, which will be described later; but they will serve as diagrams to illustrate a description of the second current-meter. *m m* is the mangle-motion, which causes the cylinder C to reciprocate and bear alternately against the two tangent-wheels *t t*. These wheels are mounted in a common swivelling-frame,

which ordinarily is kept vertical by the weights X X, but which may be inclined by a force due to any cause tending to turn the beam B. Now the turning-power of the weights X X varies as the sine of the inclination; while the turning-power of a force acting downwards applied to the point p varies as the cosine of the inclination; therefore the beam will set itself at such an angle that the tangent of the inclination is proportional to the force. If, therefore, the point p of the beam can be pulled downwards by a force which is proportional to the strength of the current, an electric meter will be the result. The coils shown in the diagrams, which belong to the energy-meter, must be removed and replaced by an electromagnet and armature of peculiar construction. Let there be an electromagnet with pole-pieces a certain distance apart, and let there be between them a wedge of iron at its narrow end increasing in thickness or width rapidly, and towards its thicker parts much more slowly; then, on moving such a wedge forwards between the poles, but without touching them, it will at first facilitate by its movement magnetic induction at a great rate; and as it fills up the space, even though the induction through it is greater, yet the increase of that induction is less. Now, as the rate at which magnetic induction is increased by movement measures the force with which such a wedge is pulled forwards, the wedge will, if suitably formed, experience a force with a given current-strength which is less as its entrance is greater, except over a small space near its starting position, where the force should, if possible, be infinite. Also, if the wedge is fixed in position and the current made to vary, it will, so long as the magnetic limit is not approached, experience a force which varies as the square of the current; therefore, if the motion of the wedge is resisted externally by a force which varies as its displacement, it will enter to such an extent that the amount of its entrance is proportional to the current. Let such a wedge be carried by the beam B, so that when it is at its zero position the beam is horizontal; then the inclination of the beam will be greater when the current is greater, and, except with very weak currents, may be made to vary so that its tangent is proportional to the current. The same principle might be applied in another way by causing rotation instead of linear movement of

the armature to facilitate induction, and by resisting such motion by a pendulum-weight as before, or by a hair-spring. The armature then would have to be shaped something like an S, and adjusted experimentally so as to give, except with very small currents, a deflection whose tangent is proportional to the current. In Sprague's or Edison's electrolytic meters (the only ones of which I have heard which can lay any claim to being called current-meters at all) a portion only of the current is sent through the meter, and the rest passed by in a shunt. Now, if it were certain that the same proportion of the whole current always passed the meter, there would be no objection to such a course; but as a rise in temperature makes an electrolyte a better, and a metal a worse conductor, any electrolytic meter combined with a shunt would have a tendency to show too much in warm weather or if warmed by the current. If, again, there is any polarization, and that polarization is not strictly proportional to the current, then another error will be introduced. It would seem therefore necessary, if accurate indications are required, to make the whole current pass through an electrolytic meter.

Electric-Energy Meters.

Since the energy expended by an electric current between any two points is equal to the current multiplied by the difference of potential of those points—that is, to the main current multiplied by a shunt current passing in a wire of high resistance between the two points—an electric-energy meter may be made by combining two electric-current meters, which take account of the direction in which the electricity passes, in such a way that the first integrates the main-current strength, and that the mangle-motion of the second is driven by the integrating-cylinder of the first: then, if the needle of the second is deflected by the shunt current, the rotation of the second cylinder will give the integral of the energy expended. This is obvious; for the rate of rotation of the second cylinder is proportional to its rate of reciprocation multiplied by the tangent of the inclination of its tangent-wheel—that is, to the strength of the current in the first machine multiplied by the strength of the current in the second; so its rate of turning is proportional to the rate at which energy is being expended,

and its whole rotation is a measure of the total energy. If at any time either the main or the derived current, but not both, changes sign, then the second cylinder will begin to turn the other way, showing that the current is not doing work in the portion of the conductor between the points, but is being caused to flow by an action of some kind taking place in that portion. If both currents change sign, then, as before, work is being done; and though the first machine is working backwards, the second is working forwards. A combination of two machines, as described, would integrate both the current and the energy. A more simple and practicable machine for integrating energy alone is shown in figs. 11 and 12. The integrating mechanism has been already described; the electrical principles employed must now be explained. If two wires, one conveying the main current and the other the derived current, are near one another, they will attract or repel one another with a force which is proportional to the product of the two currents—that is, to the energy being expended; but if the wires are allowed to move, the force will depend also on the position. The question then is, how can the wires be so arranged that the force exerted may be used to incline the tangent-wheels and yet be independent of their motion. The arrangement of solenoids shown in section in fig. 12 is a complete and perfect answer. S_1 and S_2 are two fixed solenoids concentric with one another; and the main current is made to pass through each in the same direction. S_3 is a solenoid made of a very great length of fine wire, preferably of aluminium silver, as suggested by Mr. Imray; and the upper half is wound in one direction and the lower half in the opposite direction; and the derived current is made to pass through it so as to pass in the upper half in the same direction as the main current passes in the fixed solenoids, and in the lower half in the opposite direction. This solenoid is hung in the annular space between the fixed ones by a band passing over the arc of the beam B. The tubes within and without the fixed solenoids and the rings above and below them, all of which are shown dark in the figure, are made of iron, and may or may not be used according as the currents employed are in general weak or strong. But whether the tubes are or are not retained, the use of the rings has certain advan

tages, which I now proceed to explain. Fig. 13 is a diagram taken by iron filings, which shows the distribution of the lines of force due to the fixed solenoids alone, without the tubes or rings. Here the lines of force cut the walls of the solenoid at an oblique angle, so that the force, which is at right angles both to the wires and the lines of force, tends to stretch the movable coil, and only a portion of it is effective in dragging down the solenoid : moreover the lines of force are very widely distributed over the solenoid, so that, unless it is of very great length, the upper part will leave by its motion many lines. It is true that on the lower end the movable solenoid will, when at its central position, enter as many lines in an element of motion as it leaves at its upper end ; but after any considerable movement the upper end will leave many more than the lower end enters ; and the force, as it is proportional to the number of lines enclosed, will become less as the solenoid moves from its central position. This will be referred to again later. Now the iron rings act as traps, so to speak, and catch nearly all the lines of force which without them stray over so great a space. Fig. 14 shows the field produced when the iron is present. It will be seen at once that nearly the whole of the induction takes place across a very narrow band of the solenoid, and that the lines of force, where they cut the solenoid, are nearly horizontal; so that practically the whole of the force developed tends to drag the solenoid downwards, instead of being partly spent, as before, in producing a stretching strain. The consequence is that the movable solenoid may be made very much shorter than would be necessary if no rings were present. The tubes, having a higher coefficient of induction than air, merely serve to increase the number of lines of force, rather than affect their distribution.

If a movable solenoid, arranged as described, is hung by a band passing over the arc of the beam B, then the turning moment due to a down-pulling force is, within certain limits, constant, while the force restraining motion varies as the sine of the inclination of the beam; but had it been hung from the point p, the turning moment would have been proportional to the cosine of the inclination, and the tangent of the inclination would have measured the force. What is wanted

is to make the tangent of the inclination proportional to the product of the two currents; and, as explained, this could be attained by using a long solenoid hung from the point p. But such an arrangement causes a double inconvenience; for not only is a long solenoid itself inconvenient, but the fact that it is hung from an arm and not from an arc causes a lateral shifting of the solenoid when the beam B is inclined, thus necessitating a wider annular space for it to pass through. Now the use of a comparatively short solenoid hanging from an arc introduces two errors which are almost absolutely equal and opposite. The error due to the arc is an increase of moment in the ratio of the cosine of the inclination of the beam to 1; that is, the error is equal to the versed sine of the inclination; and, like a thing that increases as the square of a quantity, it is at first quite inappreciable, and it increases in amount with increasing speed as the quantity grows. Now the error due to a short solenoid, such as shown in the figure, is at first nothing; for a given movement will cause the solenoid to enter as many lines of force at one end as it leaves at the other, but as it gets displaced it enters rather fewer than it leaves; and this difference in the number of lines of force increases in amount with increasing speed. Now, if the proportions are so taken that when the inclination of the beam is a little less than the greatest amount permitted to it the actual magnetic error is equal and opposite to the versed-sine error, then, since each is a quantity which grows according to the same kind of law, those errors will be always approximately equal, and their differences very small compared with the errors, and absolutely inappreciable in comparison with the quantities of which the errors themselves are small. The geometrical representation (fig. 15) makes this clearer. The two sets of errors may be considered as ordinates of two curves drawn to the same abscissa. The point p, where the curves intersect, corresponds to that inclination at which the two errors are made equal, and the origin O to the central position. Since both errors are of a kind which are inappreciable at first, the two curves will have the axis of x as a tangent; and since the two errors are of a kind which grow in the same kind of way, *i. e.* at first slowly, and at an increasing rate as they grow, the curves must be nearly similar;

and since they have the common point p, they must be nearly identical. The distance between the curves at any part gives the actual error there; and this being small in comparison with the ordinates at that part, is inappreciable in comparison with the whole distance of that part from the line $z z$. In the particular case the ordinate $p\,m$ is about 4 per cent. of p Q; so the actual error may be safely neglected. But, finally, should there be any error that can be detected at all, such error may be almost entirely eliminated by putting a few extra turns of wire near the ends or the middle of each half of the movable solenoid, according as the curve of the magnetic error between O and p is below or above the curve of the versed-sine error.

Assuming the truth of what is stated in the last paragraph, we find the tangent of the inclination proportional to the rate at which energy is being expended. But the speed of rotation of the cylinder is proportional to the tangent of the inclination; therefore the number of turns of the cylinder, given by the counting-mechanism in the box over the cylinder, is a measure of the total energy expended. As in the other energy-meter, so in this, if the electric current is helped at any time instead of being used, then the integrating-cylinder will turn the other way, and take off from the record an amount which is a measure of the work expended on the current.

There is a point about the solenoid energy-meter which is worthy of notice. The movable solenoid has an equal number of turns in opposite directions; so it is independent of the magnetic field in which the instrument is placed, and so this meter may be used in workshops or near dynamo-machines without its action being interfered with. For the same reason, when used in houses as gas-meters are for gas, it will be impossible for the householder to tamper with its indications by placing magnets round the instrument.

When very powerful currents are employed, it is well to shunt a certain proportion of the main current past the meter, or, when the electromotive force is very great, to introduce into the secondary circuit resistance-coils. To prevent waste of clockwork energy or of electricity, the main current is made to pass round a subsidiary electromagnet whose armature allows the clockwork to go only when the main current is passing. This armature also, on being attracted, completes

the secondary circuit, so that the derived current can only flow when the main current is passing.

The meter may be used as an energy measurer or indicator (not meter) with advantage when setting the carbons of an electric arc. If the two poles are made to touch, though the current is enormously increased, the energy is reduced, owing to a greater falling-off in the difference of potential between the poles. As the carbons are gradually separated the current diminishes, but the difference of potential increases in a higher ratio; so their product increases; that is, the energy expended, and so the heat and light produced, increases. This increase is shown by an increased inclination of the beam. After a time a point is reached at which the current decreases in the same ratio that the difference of potential increases; at this point the inclination of the beam attains a maximum; beyond this the decrease of the current is in a higher ratio than the increase in the difference of potential, so the energy, heat, and light fall off, as is indicated by the diminution of the inclination of the beam. If, therefore, the carbons are placed so that the inclination of the beam is a maximum, then the best effect is being obtained. In the same way, if the current is being employed to drive a machine, the most effective speed for that machine may be found by observing at what speed the inclination of the beam is greatest.

The various meters described depend for their numerical results on two things—(1) the horizontal intensity of the earth's magnetism, (2) the force of gravity. The indications of the first current-meter are inversely proportional to the horizontal intensity, and of the first energy-meter to the square of the horizontal intensity. Each of them is disturbed by changes in the direction of the earth's magnetism.

The second current-meter and the second energy-meter are independent of the magnetic field altogether. Their indications vary inversely as g when the clockwork is regulated by a balance-wheel, or inversely as $\sqrt{g}$ when a pendulum-clock is used. This dependence on gravity is a point of very great importance; for over any one country gravity does not change appreciably, nor does it matter in what direction the machine is placed so long as it is level. By screwing the weights X X up or down, so as to decrease or increase the influence of

gravity on the meter, its indications may be regulated to a standard measure. Therefore, in making the coils, there is no necessity to count the number of turns exactly, or to lay them with the utmost accuracy: they may be wound in the ordinary way, and then a hundred machines or more connected together, with the main circuits in series and with the derived circuits in series, and a current sent from a suitable source through each series; then, if there is one meter which has been standardized by careful experiment, all the rest can be regulated, just as clocks are, by screwing down the weights X X of those that are going fast, or screwing up the weights of those that are going slow.

If in the foregoing paper any of the apparatus is not as fully described as it might be, I must plead as an excuse an endeavour to occupy a reasonable space with an account of what is essentially one invention.

III. *Apparatus for calculating Efficiency.* By C. Vernon Boys, *A.R.S.M., Demonstrator of Physics at the Normal School of Science, South Kensington**.

[Plate IV.]

In a previous paper I have shown how work done in an engine or transmitted by shafting or belting, or expended by an electric current, or how the quantity of electricity which has passed in a conductor during any time, may be automatically measured and integrated or recorded. The present paper refers to apparatus for dividing rates of growth of two integrals so found one by the other, and continuously recording the quotient. Before describing any of these machines, it may be well to give an example showing an application of a divider to some useful purpose. Let there be a steam-engine driving a dynamo-electric machine, which is employed to produce an electric light. Steam does work on the piston of the engine, which may be integrated as already described. This is the work put in. The electricity does work in the electric arc and in the conducting wires, which may be

* Read January 28, 1882.

integrated. This is the work taken out. If after any time, say one hour, the work taken out is divided by the work put in, the quotient will represent the average efficiency of the engine and machine combined during the hour. In like manner, if the readings are taken after a minute, the quotient will give the average efficiency during the minute. If instead of a minute an indefinitely short period of time is occupied, then the quotient obtained will give the true efficiency *at* that time. Now, if by mechanism or otherwise a curve can be drawn in which the ordinates represent the true efficiency, while the abscissæ are time, then an inspection of the curve will show exactly how well the machines have done their work at every moment, and the highest points will indicate the time at which the best results have been obtained. What is wanted in practice is not a curve giving the true efficiency as above described, because work is not put into an engine uniformly, but intermittently, but a curve showing the average efficiency for the last few seconds or minutes as the case may be; and it is this that the mechanism I am going to describe accomplishes. If one of the integrals represents time, and the other work done in an engine, then the curve gives the continuous value of the horse-power per hour; or if one integral represents turns of a dynamo-machine, while the other represents electric current or electric energy, then the curve gives current-quantity or current-energy per turn. Or, generally, if two things are turning, either or both at a variable rate, a dividing machine will give the ever-varying value of the quotient of one by the other.

I have made use of two principles in the construction of dividing machines, which may therefore be classed under two heads. In the first class a pointer, if at a wrong position on the scale of quotients, moves towards its right place with a speed proportional to its distance from it: its motion is therefore of a logarithmic nature. In machines of the second class a pointer, if at a wrong position on the scale of quotients, changes its speed of moving towards its right position with a speed proportional to its distance from it: its motion therefore is of an harmonic nature. In either case the movement of the pointer may be made to trace a diagram on a travelling band of paper. I shall describe one logarithmic, and three harmonic dividers.

Logarithmic Divider.

For this a pair of wheels incapable of steering are required—that is, wheels which when turned while their edges are in contact with a surface are compelled to move forward, but which at the same time are perfectly free to move laterally. Disks with smoothly milled edges very imperfectly fulfil these conditions ; but an outside smoke-ring, such as is described in the smoke-ring integrator, *anteà*, p. 10, should answer this purpose well. Let two such smoke-rings be mounted on a common axis, but so that each may revolve independently of the other ; let there be a disk so supported that its plane is parallel to the common axis, and so that its own axis would if continued meet the other at a point midway between the two smoke-rings ; moreover, let the axis of the disk be carried by an arm in such a manner that it is capable of moving in a direction parallel to the plane of the disk, but inclined at a small angle to the common axis of the smoke-rings. Fig. 1 shows the arrangement in its central position : A A is the common axis, $S\ S_1$ are the smoke-rings, and D the disk ; the dotted line shows the line of travel of the axis of the disk. If while the disk is in its central position the two rings $S\ S_1$ are caused to revolve at equal speeds in opposite directions, then the disk merely turns, and there is no further result. Let the direction of motion be that shown by the arrow.

Now let the ring S_1 begin to revolve faster than S, then the centre of the disk D would, if free, begin to move downwards with a speed equal to half the excess; but it is incapable of moving vertically downwards; yet it may move down the slope indicated by the dotted line. Now, as the rings $S\ S_1$ in no way interfere with the lateral movement of the disk, its centre will move down the slope till it reaches such a point that the ratio of the distances of the point from the two rings is equal to the ratio of the speeds. It will be necessary to show that what is true when the produced axis of D intersects A A, is equally true when it has so far moved up or down the slope as to cause a considerable displacement. Let the centre have moved down to c, fig. 2, and let $S\ S_1$ be the points on the disk touched by the two smoke-rings, and let $c\,p$ be the perpendicular on $S\ S_1$ from c. Now, if $S\ S_1$ are turning with

speeds proportional to the lengths $S p$ and $S_1 p$, then the centre will have no tendency to move up or down. The motion of S about c as a centre may be resolved into two:—one, an upward motion, proportional to $S p$ (and this motion must, from the mechanical construction, be the same in the disk and in the ring); and the other, a lateral motion, proportional to $p c$, with which the ring in no way interferes. In a similar way, the motion of S_1 may be resolved into two—a downward motion proportional to $S_1 p$, and a lateral motion proportional to $p c$. The downward motion must be common to the disk and ring, while the lateral motion is free. It is clear then, if the rings move with speeds in the ratio $S p : S_1 p$, that the centre c will have no up or down tendency ; and if the rings are not moving with speeds in the ratio $S p : S_1 p$, that the centre c will move up or down the slope with a vertical speed proportional to the distance of the point p from a point which does divide $S S_1$ in the ratio of the speeds of the smoke-rings. If θ is the inclination of the dotted line, then c will move along this line with a speed equal to cosec θ times its vertical speed, and p will travel along $S S_1$ with a speed equal to cot θ times the vertical speed of c. Should one disk ever stop and change the direction of its motion, then c must move along the slope till it is immediately under the ring, and move beyond till it arrives at such a position c_1 that $S p_1 : S_1 p_1$ is the ratio of the speeds.

Let the two smoke-rings be turned by two integrating machines as already described, then either or both may be going at a variable speed. There must at every moment be some point x in the line $S S_1$ such that $S x : S_1 x$ is the ratio of the speeds. This point will sometimes coincide with P, at which times C will be stationary; it will generally, however, be distant more or less from P, in which case P will pursue it wi h a speed proportional to its distance from it. If the arm which carries C carries also a pencil bearing against a uniformly travelling band of paper, then the curved line drawn will show what has been the efficiency, horse-power per hour, or whatever it was set to find during any period of time. The travelling band would have to be ruled across with lines showing time, and longitudinally with lines showing ratios, the scale being of the kind shown in fig. 3.

If the slope or the direction of motion had been in the opposite direction to that shown, then p, instead of approaching its places, would have fled from it with a speed proportional to its distance from it.

I think it possible that the logarithmic divider might be applied to solve some difficult problems; for while in action the inclination of the path of the centre c to the line $S\,S_1$, or the position of either ring on their common axis, may be changed in any way without interfering with the freedom of the motion of c.

Harmonic Dividers.

All harmonic dividers depend on the steering-power of wheels, an action which renders wheels of ordinary construction useless in the case of the logarithmic divider. The steering action, however, is not determined by any direct effect, as in the case of my cart integrating-machine, or in the more familiar case of a common bicycle, but depends on an intermediate action, and is in this respect exactly similar to the steering arrangements in that most beautiful and ingenious machine the "Otto" bicycle. In this the rider produces a difference in the speeds of two wheels, one on each side of him; the angular deviation therefore is the integral of the difference in speed between the two wheels, while the linear deviation from the original straight course is the integral with respect to the distance run of the sine of the angular deviation. The method of adapting this principle is exactly analogous to the case of the disk-cylinder integrator. That machine was developed in this way:—Take a cart integrator running on fixed ground, remove the whole of the cart except its steering-wheel, which fix in position, then give it movable and cylindrical ground to run on; a disk-cylinder integrator will be the result. In this case do away with the whole of Otto's machine except the two wheels, fix them in position, and give them each a movable floor to run on. Fig. 4 is a side view, and fig. 5 is a plan, of a machine of this kind. $A\,A_1$ are the two steering wheels mounted independently on a common axis; $B\,B_1$ are a pair of disks geared together by their edges, and they form the movable floors for the disks A A to rest upon. $c\,c_1$ are the supporting wheels of a frame F, and

are capable of running on rails parallel to the common axis of $A A_1$. The frame F carries a block D swivelled on a vertical axis passing through the centre of both F and D. The axes of $B B_1$ are supported by D. If $A A_1$ are caused to turn with speeds proportional to their distances from the centres of $B B_1$ and in the same direction, $B B_1$ will revolve at equal speeds in opposite directions, and neither D nor F will be affected; but if either A or A_1 is made to revolve a little faster than is due to its central distance, D will begin to turn in its swivel-frame. But no sooner does D begin to twist, than the disks $A A_1$, which previously were describing circles on $B B_1$, tend to move in spiral paths, the faster one receding from, and the slower one approaching, the centres of the disks $B B_1$ on which it is moving. But as $A A_1$ are incapable of any movement but rotation, while the disks $B B_1$ can, from the nature of their support, accommodate themselves to every kind of movement except one of lateral translation, therefore the combination c, F, D, B, and B_1 will move longitudinally till the central distances of $A A_1$ are proportional to their speeds; but, unfortunately, by this time the obliquity of the block D has become a maximum, and therefore its rate of longitudinal travel is a maximum also. It therefore travels on and introduces an error of position on the opposite side, which is corrected as before; and so the frame F oscillates on either side of its correct position. The motion may be considered more exactly in this way:—The rate at which D twists is proportional to the error of F, while the rate at which F corrects its position is proportional to the amount of twist of D: this expressed mathematically gives the equation $\frac{d^2y}{dx^2} = -y$, the solution of which is $y = \sin x$ or $y = \cos x$. The motion of both D and F therefore is harmonic. An exactly analogous case is that of a heavy body moving under the influence of a force which varies with the displacement, the movements of F being equivalent to that of the heavy body, while the rate at which D twists represents the force. Of course in the dividing-machine described we have nothing to do with inertia or with a resisting force; but the movements are the result of an action of pure rolling, and it so happens that they follow exactly the same law as the movements of a vibrating heavy body. This

view of the subject removes all difficulty in discovering what will be the action during either slow or very rapid variations in the ratio of the velocities. Let the dynamical equivalent be a heavy magnetic needle balanced in a magnetic field. Then the direction of the field corresponds to ratio of velocities, and the motions of the needle to the motion of the frame F. As has been shown in the case of a constant ratio, an error of position of F at starting causes F to oscillate on either side of its correct place, just as a displacement of a magnetic needle causes it to oscillate. Now suppose F to be in its correct position and then the ratio to change slowly (that is, slowly compared with the time of an oscillation); then the frame F will move slowly also, always being in the correct position, because during a slow change in the direction of the magnetic field a balanced needle follows the change without oscillation. Next suppose the ratio to alternate rapidly—that is, rapidly compared with the time of an oscillation, as, for instance, is the case when a steam-engine is made to do work uniformly, for work is put in intermittently and taken out gradually; then the dividing-machine will steadily show the mean value, and will take no account of the rapid variations in ratio, because a heavy magnetic needle subjected to rapidly alternating currents, which produce rapid variations in the direction of the magnetic field, is unaffected by these currents, but steadily maintains its position in the mean direction of the field. The most complex possible case is a combination of rapidly alternating and slowly changing ratios with occasional sudden changes. The first two are properly considered by the machine, while the sudden changes merely cause the frame F to oscillate on either side of its correct position. As in the case of the logarithmic divider, so here; a curve may be drawn on a travelling band of paper by a pencil attached to the frame.

A more simple arrangement is shown in fig. 6, where the disks B B_1 and the frame and block are replaced by a sphere S with its axis horizontal mounted in a horizontal ring R, and where this ring is supported in a crutch *c* which is capable of moving round on a vertical axis. Thus, when R is horizontal, the sphere can turn independently round three axes at right angles to one another. Then, if the disks A A_1 touch

the sphere in points 90° apart, the ratio of their speeds will be measured by the tangent of the inclination of R, while the deviation of c will correspond to the obliquity of the block D in the last machine.

The most simple harmonic divider that I can imagine is made by mounting, as shown in fig. 7, two iron cones with their bases adjacent, and with the lowest generating line in each horizontal and in one straight line. Then, if a magnetized steel reel is hung on and the two cones are turned, the reel will travel about and find the ever-varying value of the ratio of their speeds. The method of attaching a recording-pencil is too obvious to need description. If the two cones were placed so that their bases were turned away from one another instead of being adjacent, then the reel would change its speed of moving *away* from its correct position with a speed proportional to its distance from it. This kind of action could only exist, of course, for a very short time.

Whether dividing-machines are likely to be of general value for practical or experimental purposes, it is difficult to say; but there can be little doubt that cases might arise in which some machine such as I have described might be used with advantage.

IV. *On the Violet Phosphorescence in Calcium Sulphide.* *By* Captain W. de W. Abney, *F.R.S.**

In some investigations in photography it became necessary that I should study the phenomenon of phosphorescence exhibited in calcium sulphide, such as is employed in Balmain's paint. And as one or two points of interest arose which have not (as far as I am aware) been described before, I have thought it might be of interest to lay the subject before the Society.

The phosphorescent light, which is a peculiar violet, can be generated, if I may use the term, by day-light or candle-light —by the former fairly brightly, and by the latter only feebly, for reasons which will appear. In order to gain strong phosphorescence, the light from a magnesium-ribbon or the electric

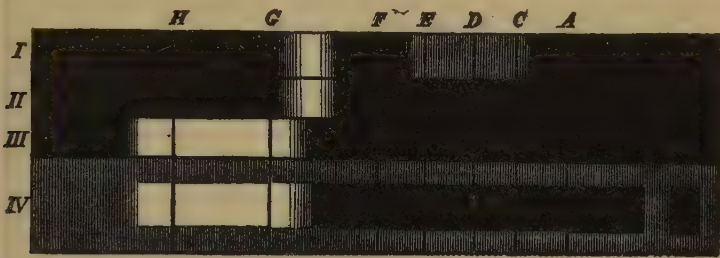
* Read January 28, 1882.

light should be employed. Mr. Warnerke has shown that $\frac{1}{8}$ inch of ribbon of the former is sufficient to excite phosphorescence to the maximum point that can be obtained from light of that brilliancy. Light of greater brightness, however, seems to excite it even more strongly. In a communication made to the Society by Lieut. Darwin, R.E., he gave the formula for the decrease of phosphorescence after excitation, from which it will be seen that it very rapidly diminishes in brilliancy.

My first experiment was to determine the spectrum of the emitted light; and this I observed with a small spectroscope; and the emission-spectrum is shown in I, figure opposite. It will be seen that to the eye the greatest luminosity is between G and F, and a feebler one extending from between E and F as far as the eye can recognize colour of low intensity towards the red. It became a matter of curiosity to know if any rays lay beyond the violet; and for this purpose an Iceland-spar prism and quartz lenses to the collimator and camera were brought into requisition, together with extremely sensitive photographic plates. Glass was spread with a layer of this sulphide and held together by paraffin as a substratum; the phosphorescence was excited by the electric light, and the tablet held in front of the slit. The exposure lasted one minute, when the phosphorescent tablet was again excited, and used as a source of light as before. After forty such excitations the photographic plate was developed; and a band (shown in II) was registered, which absolutely coincided with the band already registered in the visible spectrum. There was no trace of any radiation having wave-lengths in the ultra-violet. Whether there is any radiation below the red is a moot point; but from the gradually increasing brightness of the spectrum in the yellow, it seems probable that there is such.

The next point to ascertain was the part of the spectrum which excited phosphorescence. A tablet similarly prepared was exposed to the spectrum of the electric light, which showed carbon-bands strongly just above H, and also in the violet near G. A sensitive photographic plate was placed in contact with the tablet, and allowed to remain in contact 40 seconds, after which it was developed. III shows the locality of the spectrum by which phosphorescence was ex-

cited. This agreed absolutely with the visual observations. The exact locality was fixed by the carbon-bands above alluded



to, and also by comparing it with a sensitive photographic plate exposed in the ordinary manner. It will be noticed that the ultra-violet rays do not seem to cause phosphorescence in this case.

It now remained to register those rays which destroy the phosphorescence. This was effected in the following manner:—A tablet was first excited, and after half a minute exposed to the spectrum: those rays which destroyed phosphorescence were distinctly visible, as were also those which excited it. The tablet was placed in contact with a sensitive plate and developed. The wave-lengths were determined by placing a liquid in front of the slit and noting the place where the known absorption-bands in the infra-red region occurred, which is here shown by these localities remaining of the same luminosity on the tablet surrounding the impressed spectrum. The rays which destroy phosphorescence of this description are shown in IV. It will be noted that in the infra-red region is a portion which does not destroy it. When the wave-lengths of this are compared with the wave-lengths of the exciting portion about G and H, it is found that they are octaves one to another. (In the figure the infra-red region is much compressed, owing to the spectrum used being a prismatic spectrum.

This fact appears remarkable and worthy of note. My own impression is that another band below this may also be traced; but as it was not shown upon the photographic plate, I have not mapped it. Such a band would probably be another octave below the second band. It should be noted that the infra-red band apparently is of the same luminosity as the general lumi-

nosity of the plate, and that these rays only feebly excite the plate.

I have endeavoured to make out any spectral difference in the light excited about H and about G, and have failed to obtain evidence as to any alteration in colour. It seems indifferent whether phosphorescence be excited by the indigo or by the violet rays.

I am at present engaged upon other phosphorescent material.

V. *On the Refractive Index and Specific Inductive Capacity of Transparent Insulating Media. By* J. Hopkinson, *D.Sc., F.R.S.**

One of the deductions from Maxwell's electromagnetic theory of light is, that the specific inductive capacity of a medium is equal to the square of its refractive index. Another deduction is, that a body which is opaque to light, or, more generally, to radiant energy, should be a conductor of electricity. The first deduction appeared so clear an issue that many experimenters have put it to the test. The results may be briefly summarized thus:—Some bodies (such, for example, as hydrocarbon oils † and paraffin-wax) agree with Maxwell's law so well that the coincidence cannot be attributed to chance, but certainly points to an element of truth in the theory: on the other hand, some bodies, such as glass ‡ of various kinds, fluor-spar §, Iceland spar §, and the animal and vegetable oils ||, have specific inductive capacities much greater than is indicated by their refractive indices.

How do these latter results really bear on Maxwell's theory? The facts are these. Taking the case of one substance as typical, the refractive indices of light flint-glass are very accu-

* Read February 25, 1882.

† Silow, Pogg. *Ann.* 1875, p. 382; 1876, p. 306. Hopkinson, Phil. Trans. 1881, part i. p. 371.

‡ 'Cavendish Researches,' edited by Clark Maxwell; Schiller, Pogg. *Ann.* 1874, p. 535; Wullner, *Sitz. k. bayer. Akad.* 1877, p. 1; Hopkinson, Phil. Trans. 1878, part i., 1881, part ii.

§ Romich and Nowak, *Wiener Sitz.* Bd. lxx. part 2, p. 380.

|| Hopkinson, Phil. Trans. 1881, part ii.

rately known, the period of disturbance ranging from $\frac{1}{4{\cdot}0 \times 10^{14}}$ second to $\frac{1}{7{\cdot}6 \times 10^{14}}$ second; the specific inductive capacity is known to be about 6·7, the time of electrical disturbance being from $\frac{1}{17000}$ second to a few seconds. If from the observed refractive indices we deduce by a formula of extrapolation the refractive index for very long waves, we find that its square is about one third of 6·7. There can be no question about the accuracy of the observed refractive indices; and I have myself no doubt about the specific inductive capacity; but formulæ of extrapolation are always dangerous when used far from the actual observations. If Maxwell's theory is true, light flint-glass should be perfectly transparent to radiations having a wave-period of, let us say, $\frac{1}{17000}$ second; because this glass is sensibly a perfect electrical insulator, its refractive index for such waves should be about 2·6. Are there any facts to induce us to think such a thing possible? It is well known that in some cases strong selective absorption of light in the visible spectrum causes what is known as anomalous dispersion; that is to say, the body which presents such selective absorption of certain rays has a refractive index abnormally low for waves a little shorter than those absorbed, and an index abnormally high for waves a little longer than those absorbed*.

Light flint-glass is very transparent through the whole visible spectrum, but it is by no means transparent in the infra-red. If the absorption in the infra-red causes in light flint-glass anomalous dispersion, we should find a diminished refractive index in the red. We may say that we have a hint of this; for if we represent the refractive indices by the ordinates of a curve in which the squares of the reciprocals of the wave-lengths are abscissæ, this curve presents a point of inflection†. In the part corresponding to short waves it is concave upwards; in the part corresponding to long waves it is concave downwards: the curvature, however, is very slight. Does it not seem possible, looking at the matter from the purely optical point of view, that if we could examine the spectrum below the absorption in the infra-red, we should find the effect of anomalous dispersion, and that the refractive index

* 'Theory of Sound,' by Lord Rayleigh, vol. i. p. 125.

† Proceedings of Royal Society, 1877.

of such long waves might even be so high as 2 6? To test this experimentally in a conclusive manner would probably not be easy. Perhaps the best chance of finding how these long waves are refracted would be to experiment on the rays from a thermopile to a freezing-mixture. Without an actual measurement of a refractive index below all strong absorption, it cannot be said that experiment is in contradiction to the Electromagnetic Theory of Light; for a strong absorption introduces a discontinuity into the spectrum which forbids us from using results on one side of that discontinuity to infer what they would be on the other side.

VI. *Water-pipes that do not burst with Frost.* *By* C. Vernon Boys, *Demonstrator of Physics, Normal School of Science, South Kensington**.

During the severe weather of last winter, Mr. L. S. Powell proposed to me a scheme for preventing the possibility of water-pipes bursting through frost; and I have since learnt that Mr. Mangnall, of Manchester, independently hit upon the same idea. As far as I can remember, there were some letters in the 'Times' describing the use of india-rubber pipes containing air inserted in the service-pipes. This would obviously prevent pipes from bursting; for the pressure is of a nature that is relieved by a comparatively small expansion; and this the india-rubber tube allows to take place in the surrounding water when it collapses. There is, however, one serious objection to this, which is the possibility of the detachment of one end of the flexible tube, in which case a rush of water might cause it to accumulate in one place and obstruct the passage.

Mr. Powell's plan is to make the piping elliptical—either before it is laid, in which case it may be made of that form originally or by passing round pipe through rollers, or afterwards, when suitable hand-squeezers will effect the result without the necessity of removal. As will afterwards be seen, it is not necessary that the pipe should be elliptical throughout; if

* Read November 12, 1881.

left round under staples and in other inaccessible places, the adjacent elliptical portions ensure safety. The principle, of course, is obvious. As is well known, the Bourdon pressure-gauge depends on the fact that the area of an elliptical pipe is less than that of a circle of equal perimeter: therefore during increased pressure its section becomes more circular; increased circularity of section produces diminished curvature in the form of the pipe; and so the movements of the end of the pipe are used to measure pressure. Thin brass is used for this purpose, and is so elastic that it returns to its original form when the pressure is removed; and so an indefinite number of increments and decrements of pressure may be measured by it. The case of the elliptical water-piping is different. Here there is not a definite pressure to withstand, but a definite increase of volume; and, moreover, if this increase of volume is resisted, a practically infinite force arises to break down the resistance. The question then is, how best to allow of this increase of volume. The method of the indiarubber pipes I have already mentioned. The other plan is to make them of an elliptical or other-than-round section. There is, however, far more in this suggestion than one would be likely to see at first. Consider the case of a round pipe in which water is beginning to freeze. Increase of volume must take place somewhere. No pipe can be absolutely uniform in strength everywhere. So wherever a place occurs which happens to be a little weaker than the rest, no matter how little, that place will stretch, and necessarily stretch more than other places. But when a round pipe stretches, two things happen—its diameter increases and its thickness decreases; therefore, as the strength of a tube to resist bursting is inversely as the diameter and directly as the thickness, each of these effects makes the stretched portion still weaker than the neighbouring parts; therefore a round pipe under the action of frost is in a state of unstable equilibrium; the consequence is, knobs form on the pipe, and ultimately burst.

Now consider the case of an elliptical pipe, of such strength of course, as to stand the ordinary water-pressure. As before suppose some portions are weaker than others. When expansion takes place they will suffer most, and will begin to give way. But an elliptical pipe on giving becomes more circular

and this the more easily as its section departs more from the circle; so the very fact of its becoming more circular makes it less ready to change its form. In a very little while, therefore, though originally weaker, it will become as strong as neighbouring portions: therefore an elliptical pipe under the action of frost is in a state of stable equilibrium, and, instead of giving way in the bulbous manner of a circular pipe, it uniformly becomes more circular. Now the expansion of water in becoming ice is known; and therefore it is easy to calculate by compound interest how many *complete* freezings (that is, freezings from one end of the pipe to the other) any given section of piping will stand before it becomes round. Of course, in practice, the whole length of a pipe does not get frozen; yet if it were originally all of it elliptical, the unfrozen portions would be effective in preventing the more exposed parts from bursting; because as soon as the exposed portions have become rounder than the rest, the latter, and not the former, will yield. If two places in the pipe become completely frozen through and then the intermediate portion freezes, it is true that parts beyond the frozen plug will have no effect.

Mr. Powell and I tried a series of experiments on the subject to see if, in practice, the pipes behaved as we expected. We obtained a quantity of $\frac{3}{4}$-inch lead pipe, about $\frac{1}{10}$ inch thick, and some thin composition pipe of the same size. The piping was cut into lengths of about three feet; half of them were squeezed into an approximately elliptical form, and the rest left circular in section. The degree of ellipticity was such that the major axis was a little more than twice the minor axis. One end of each pipe was squeezed together and soldered. Into the other ends brass plugs cut with a sharp thread were screwed while hot, having been previously smeared with a cement of rosin, beeswax, and red-ochre. After these plugs were inserted and while still hot, the lead was, as an additional precaution, squeezed over a narrower portion of the plug above the screw-thread. In each plug a hole had been drilled and tapped. Through these holes the pipes were filled with water; and then iron screws, with washers of leather boiled in beeswax and tallow, were used to make a tight joint. The pipes were then all laid together in a long box, and surrounded with

a freezing-mixture. When a short test-pipe of the same diameter showed that the water was completely frozen, the pipes were removed and thawed. The round composition pipe was burst. The round lead pipe was swollen in an irregular manner. The elliptical piping had become slightly rounder, but was perfectly uniform in shape from end to end, which was not the case when it was put in the freezing-mixture. The most noticeable thing, however, was the fact that all the unburst pipes had become good water-hammers, and this showed that leakage could not have occurred. The screws were removed, the pipes filled, again screwed up and refrozen, and this was repeated till all were burst. The round lead and the thin elliptical composition pipe burst at the third freezing, and the elliptical lead pipe at the sixth. Judging from the fact that it required three freezings to burst the round pipe, one might be led to suppose that a round pipe would last equally long under ordinary conditions, which is certainly not the case. The reason is that, under ordinary conditions, a greater length freezes at a time and more slowly; and a slight inequality arising, the expansion from a greater volume of water is concentrated on the weaker places, which therefore give way during the second, if not the first, freezing of the water.

It might be thought that, as the outer layers of ice are below the freezing-point when the pipe is being cooled, they would not act as a plastic body and accommodate themselves to the changing form of the pipe; but no doubt can remain as to their behaviour in this respect when the pipe is cooled in air; for in the freezing-mixture, where the rate of cooling must be much more rapid, such accommodation takes place perfectly, even thin composition pipes changing their form and becoming round. The apparent plasticity of the ice may depend on fracture and regelation; for if the outer layers are below the freezing-point, and a bursting-pressure is brought to bear on the compound pipe formed of lead and ice, it might yield, the lead bending and the ice cracking, and so allowing the water to penetrate the cracks and freeze in them. Whether this action takes place or not does not much matter: the result, as in the somewhat different case of glacier-motion, is much the same.

If the pipe is made of such a form that it will not become round till it has been completely frozen, say, three times, it will take a great many frosts to burst it, as those parts that do not freeze easily will protect the more exposed portions; so absolute security may be relied upon till ordinary round pipes have burst once or twice; and then the now nearly round ones may be squeezed back to their original form. The choice, then, is between two evils; either burst pipes, with the usual damage and cost of repair, or the trouble of inspection every second or third time that the neighbours find that the "thaw" has burst theirs.

We thought it possible that iron might be sufficiently elastic to return to its original form; and so we froze water in two ¾-inch iron gas-pipes, one round and one which had been flattened when red-hot. The round pipe burst the first time; the flat one did return slightly when thawed, but not enough to prevent its bursting during the second operation.

No doubt most people will not consider this proposal of Mr. Powell's a satisfactory cure for burst pipes; they would like something which could be fixed in their houses and which would be always safe without further attention. But till such a discovery is made, I think elliptical pipes give the best solution of a problem which has troubled every householder.

As the subject of this paper is of physical as well as general interest, I hope that it may be considered not unworthy of the attention of the Physical Society.

VII. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part V. *By* C. R. ALDER WRIGHT, *D.Sc. (Lond.), F.R.S., Lecturer on Chemistry and Physics in St. Mary's Hospital Medical School**.

On the Relationships between the Electromotive Force of a Daniell Cell and the Chemical Affinities involved in its Action.

102. IN accordance with the theorem stated in § 61, the E.M.F. that would be requisite to break up a given electrolyte under given conditions into the "nascent" products of electrolysis would be a constant amount, were it not that

* Read February 11, 1882.

the secondary physical and chemical actions of the electrodes, and of dissolved gases, &c. upon the nascent products give rise to the development of an amount of heat, the energy equivalent to which diminishes the work that would otherwise be done by the current whilst effecting electrolysis; so that the E.M.F. corresponding to the net electrolytic work actually done is less than the constant amount that would be requisite in the absence of these interfering circumstances; under certain conditions, the diminution in the work is so great that work is gained instead of spent, when the cell becomes an electromotor. Experiment shows that, *cæteris paribus*, the amount of diminution is less the more rapid the rate of current-flow; so that in a decomposing cell, in which, on the whole, work is spent during the passage of the current in doing electrolysis (the heating effect due, in accordance with Joule's law, to the resistance proper of the cell being left out of consideration), the counter E.M.F. set up (representing the work so spent) is of + sign, and increases in magnitude with the rate of current-flow; whilst in an electromotor, in which, on the whole, work is gained during the passage of the current, the counter E.M.F. set up is of − sign (*i. e.* is a direct E.M.F.), and decreases in magnitude with the rate of current-flow.

This decrease in magnitude, although a phenomenon well known under the name of "polarization of the cell," has nevertheless been less thoroughly investigated than is desirable. Thus, for instance, in the case of a given Daniell cell it is unknown to what relative extents the diminution is due to each of three entirely different possible causes, viz.:—first, the formation, in consequence of the electrolytic actions going on, of a stronger zinc-sulphate solution round the zinc plate, and of a weaker copper-sulphate solution round the copper plate, than were there originally; secondly, the more or less incomplete action as regards setting up E.M.F. of the energy gained by the solution of the zinc, and displacement thereby of copper from the copper-sulphate solution; and, thirdly, the somewhat analogous want of completeness in transformation into E.M.F. (and quantity of electricity jointly) of the energy gained by the transformation into ordinary copper of the nascent metal thus set free. In order to refer briefly to this possible want

of completeness in development of E.M.F., it will be convenient to term that portion of the energy due to the various actions taking place in the cell that does contribute to the setting-up of difference of potential, the "adjuvant" portion of this energy; whilst the remainder is spoken of as the "non-adjuvant" energy. Of course the non-adjuvant energy in practice makes its appearance in the form of heat developed *ab initio*, and not in accordance with Joule's law—*i. e.* not due simply to the passage of a current through a resistance.

As regards the possible non-adjuvancy of energy thus indicated, it is to be noticed that whilst the observations of numerous experimenters agree in showing that, under certain conditions, at least an approximate equality subsists between the electromotive forces actually developed in a Daniell cell, and in various analogously constructed cells, and those corresponding to the net chemical changes taking place therein (viz., in the case of a Daniell cell, the displacement of copper from copper sulphate by zinc), this approximate equality does not exist under all conditions even in a Daniell cell, inasmuch as, first, considerable discrepancies exist between the values obtained by different observers working under different conditions, and, secondly, the same cell exhibits values varying with the rate of current-flow through so-called "polarization;" whilst, on the other hand, with certain forms of cell the maximum E.M.F. developed falls considerably short of that corresponding to the net chemical action. These discrepancies and amounts of falling short appear to be in certain cases considerably greater than can be accounted for by the formation of solutions of zinc and copper sulphates &c. of different densities through "migration of the ions," thus indicating considerable extents of non-adjuvancy.

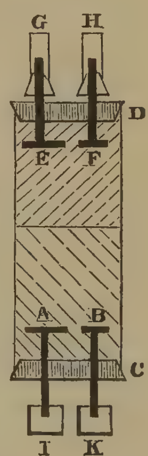
In order to obtain further information upon these points, a large number of observations have been made upon various forms of Daniell cell and allied combinations; the general results of which are that, with the normal Daniell combination (zinc, zinc sulphate, or dilute sulphuric acid, copper sulphate, copper), the amount of non-adjuvant energy with suitable plate-surfaces and with feeble rates of current-flow is insensible, but becomes very considerable with more rapid rates of flow, or with certain impure forms of metallic plate-surfaces—the non-adjuvancy

being partly due to incomplete development as E.M.F. of the energy due to the solution of the zinc, but more especially to the imperfect development as E.M.F. of that due to the transformation of nascent into ordinary copper; whilst the formation of solutions of densities different from those of the fluids originally employed also contributes to the diminution in the effective E.M.F. of the cell. With certain other forms of cell, more or less non-adjuvancy exists under all circumstances. In the following paper only those experiments referring to the normal Daniell cell are described, the remainder being postponed to a later occasion.

Experiments made to determine the total fall in E.M.F. through so-called Polarization, occurring in variously arranged Daniell Cells for definite amounts of increase in the rates of Current-flow.

103. A gravity Daniell cell was constructed (fig. 1) with two zinc plates, A and B, supported so that their upper surfaces were in the same horizontal plane, by means of stout wires passing through an indiarubber cork, C, the under surfaces of the plates, and the wires between the cork and plates, being covered with gutta percha. This cork fitted into the lower end of a wide glass tube some 4 or 5 centim. in diameter and 12 or 15 long; at the other end was a precisely similar cork arrangement, D, carrying two copper plates, E and F, of which only the lower surfaces were uncovered with gutta percha. The plates A and E were each of such size as to expose precisely 2·5 square centim. of surface, whilst the plates B and F each exposed double that area. In order to arrange the cell as a gravity battery, a concentrated zinc-sulphate solution (sp. gr. nearly 1·4) was run into the cell until half full, and then a cold-saturated solution of copper sulphate (sp. gr. somewhat below 1·2) was carefully floated on the top of the zinc-sulphate solution. In some experiments this disposition of the plates was reversed, the copper plates being lowest and the zinc plates highest; in these cases saturated copper-sul-

Fig. 1.



phate solution was first poured in, and then a lighter zinc-sulphate solution. To avoid the almost inevitable contamination of the zinc-sulphate solution with faint traces of copper sulphate which occurs when the former is poured on to the latter, no matter how carefully done, it was found more satisfactory to fill the cell half full of the zinc-sulphate solution, and then slowly to introduce the copper sulphate at the base of the cell through a U-tube passing through the cork C, the end inside the cell being drawn out to a point and bent downwards, so that the copper-sulphate solution flowed in gradually and lifted up the zinc-sulphate solution without passing into it as a jet and so more or less impregnating it with copper.

It is evident that, since A and B, E and F are respectively in the same horizontal planes, the resistance of the column of fluid between the plates, R, must be sensibly the same, whether the smaller pair of plates, B and F, or the larger pair, A and E, be employed to generate a current; either of which can at pleasure be done by simply connecting the mercury-cups G H I K, attached to the appropriate plates, with the extremities of a known external resistance. By measuring the difference of potential E subsisting between the ends of this resistance the current passing, C, is known; hence if R be known, the E.M.F. of the cell, e, is known, being given by the equation

$$e = \mathrm{E} + \mathrm{CR}.$$

The value of R can be deduced, with a fair amount of precision, from the results of two series of observations with varying currents, made, first, with the smaller, and, secondly, with the larger pair of plates, in the following way:—By dividing the actual current-strengths by 2·5 and 5·0 (the superficies in square centimetres of the plates respectively), two series of values of E for corresponding "current-densities" (rates of flow per square centimetre of plate surface) are obtained, by interpolation from which, for a given current-density D, two values, E_1 and E_2, are deduced for the smaller and the larger pair of plates respectively. The E.M.F. with the smaller pair, e_1, is manifestly

$$e_1 = \mathrm{E}_1 + 2{\cdot}5\,\mathrm{DR},$$

whilst that with the larger pair is

$$e_2 = \mathrm{E}_2 + 5{\cdot}0\,\mathrm{DR}.$$

It is evident that, when the density of the current is the same, and the surfaces of the two copper and of the two zinc plates are respectively in the same conditions, the effect on the E.M.F. caused by the passage of a current must be sensibly the same, inasmuch as the same amount of zinc is dissolved and of sulphate of zinc formed, and the same quantity of copper is deposited and of copper sulphate decomposed, per square centimetre of plate surface; so that e_1 must sensibly $=e_2$.

Hence, since

$$E_1 + 2{\cdot}5\,CR = E_2 + 5{\cdot}0\,CR,$$

it results that

$$R = \frac{E_1 - E_2}{2{\cdot}5\,D}.$$

By contrasting in this way the values of the E's obtained with various current-densities, a set of values for R are obtained, fairly concordant when the observations are carefully made and the plates of such materials as to remain in the same condition of surface throughout the experiment, or nearly so, so that on introducing a given external resistance into the circuit, sensibly the same values for the E's are uniformly obtained. With sulphate-of-zinc solution surrounding the zinc plates, and with amalgamated plates (copper as well as zinc), this permanence is more readily ensured than when dilute sulphuric acid is used (with amalgamated zinc plates), or when the copper plate is not amalgamated, but only freshly coated with electro-deposited metal. Indeed, to obtain a sufficient number of readings when dilute sulphuric acid is employed, it is preferable to discharge the cell after an hour's use and recharge it, amalgamating the plates afresh, and filling up with the same solutions as before to exactly the same levels (ensured by suitably marking the glass), so that the resistance of the cell may vary as little as possible, the temperature being so adjusted as to be sensibly the same on the average throughout. Thus the following series of values was obtained as the average result of four sets of readings alternately with gradually increasing and gradually diminishing external resistances, with a cell containing nearly saturated copper-sulphate solution, freshly electro-coated copper plates, amalgamated zinc plates, and dilute sulphuric acid of 1·045 sp. gr., the plates being reamalgamated and reelectro-coated respectively for each successive series—all the observa-

tions being reduced to the same standard as that adopted throughout this paper, viz. the average reading at 15·5 of a large number of Clark's cells taken as 1·457 volt*.

Smaller plates.			Larger plates.		
C_1.	D_1.	E_1.	C_2.	D_2.	E_2.
·001738	·0006952	·869	·00385	·000770	·770
·000960	·0003840	·960	·001854	·0003708	·927
·000509	·0002036	1·018	·000999	·0001998	·999
·0002112	·00008448	1·056	·0005195	·0001039	1·039
·0001075	·00004300	1·075	·0002136	·00004262	1·068
·0000543	·00002172	1·085	·0001085	·00002170	1·085
·0000273	·00001092	1·092	·0000546	·00001092	1·092
·00001057	·00000423	1·097	·0000262	·00000524	1·097
·00000533	·00000213	1·100	·0000108	·00000216	1·100
·00000215	·00000086	1·103	·00000535	·00000107	1·103
·00000107	·00000043	1·103	·00000215	·00000043	1·103
·00000052	·00000021	1·103	·00000105	·00000021	1·103

* The exactness of this value depends not only on how far the average of these cells is identical with the average of those which served as the basis of Clark's valuation (Proc. Roy. Soc. xx. p. 444), but also on the exactness with which the B.A. unit of resistance is determined. If this latter be too small—as appears probable from the experiments of Joule, and of the writer and Mr. Rennie (Phil. Mag. March 1881, p. 169), from the results of Rowland, and from the recent experiments of Lord Rayleigh and Prof. Schuster—the true value of an average Clark's cell is below 1·457 to the same proportionate extent: thus, if the B.A. unit be really 0·99 $\frac{\text{earth-quadrant}}{\text{second}}$, the E.M.F. of an average Clark's cell is only $0·99 \times 1·457 \times 10^8 = 1·442 \times 10^8$ C.G.S. units. In view, however, of the fact that the question of the amount and even of the direction of the error (if any) in the B.A. resistance unit is not yet absolutely settled, it is assumed in this paper that there is no error at all.

For analogous reasons the value of J is assumed, as previously, to be 42×10^6 ergs, the evidence in support of its having a higher value still being not inconsiderable; although the probability is that, if the B.A. resistance unit be only 0·99 $\frac{\text{earth-quadrant}}{\text{second}}$, J is close to $41·5 \times 10^6$. The value of χ (the electrochemical constant defined in § 7) deduced in § 9 as the most probable, viz. ·000105, is also adhered to, notwithstanding that Mascart's recent experiments (*Comptes Rendus*, xciii. p. 50) tend to indicate that this value is too large, ·0001044 representing his final result: this value is 0·8 per cent. lower than ·00010527, the mean value deduced from Kohlrausch's experiments. If J be taken $= 41·5 \times 10^6$, and χ be assumed $=$ ·0001048 (mean of Mascart and Kohlrausch's results), the value of χJ, the factor for reducing gram degrees to C.G.S. E.M.F. units, becomes

104. From these figures the following values for R are deduced—the first four determinations only of each series being employed, on account of the smallness of the differences between E_1 and E_2 in the other cases:—

D.	E_1.		E_2.		$E_1 - E_2$.	$R = \frac{E_1 - E_2}{2\cdot5 \times D}$.
	Observed.	Interpolated.	Observed.	Interpolated.		
·000770	...	·847	·770	...	·077	4·00 ohms.
·0006953	·869	...	...	·799	·070	4·03 „
·0003840	·960	...	...	·921	·039	4·05 „
·0003708	...	·965	·927	...	·038	4·11 „
·0002036	1·018	...	...	·997	·021	4·12 „
·0001998	...	1·019	·999	...	·020	4·04 „
·0001039	...	1·050	1·039	...	·011	4·24 „
·0000845	1·056	...	...	1·047	·009	4·28 „
					Average	4·11 ohms.

Taking 4·11 ohms as the average value of R, the following numbers are calculated from the above observations, the values of E_1 and E_2 being obtained by interpolation:—

Values from observations with smaller plates.				Values from observations with larger plates.			Average value of E.M.F. of cell.	Fall.
D.	E_1.	2·5×DR.	$e_1 = E_1 + 2\cdot5DR$.	E_2.	5·0×DR.	$e_2 = E_2 + 5\cdot0DR$.		
0	1·103	...	1·103	1·103	...	1·103	1·103	0
·000001	1·103	...	1·103	1·103	...	1·103	1·103	0
·000002	1·100	...	1.100	1·100	...	1·100	1·100	·003
·000005	1·096	...	1·096	1·097	·001	1·098	1·097	·006
·00001	1·092	·001	1·093	1·092	·002	1·094	1·094	·009
·00002	1·086	·002	1·088	1·086	·004	1·090	1·089	·014
·00005	1·072	·005	1·077	1·065	·010	1·075	1·076	·027
·0001	1·051	·010	1·061	1·041	·021	1·062	1·062	·041
·0002	1·019	·021	1·040	·999	·041	1·040	1·040	·063
·0004	·957	·041	·998	·916	·082	·998	·998	·105
·0007	·868	·072	·940	·798	·144	·942	·941	·162

It is evident that the values of e_1 and e_2 accord so closely

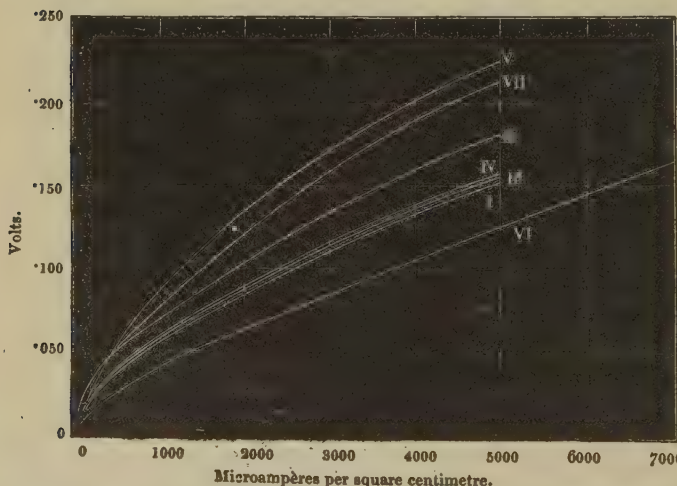
4349, or 1·4 per cent. less than 4410, the value hitherto assumed, and retained in this paper.

Prof. S. P. Thompson applies the term "Faraday coefficient" to the numerical value χ (Journ. Soc. Arts, xxx. p. 34); should this term be generally accepted, the letter F might gracefully be used instead of χ to indicate the factor, just as J is used to indicate the Joule coefficient.

that their average may fairly be taken as representing, with but little error, the E.M.F. of a cell containing copper and zinc plates in the condition of those experimented with in this instance*.

105. In various other analogous experiments the concordance was usually not quite so close as in this example, a smaller number of readings (one or two sets only) being made; but the discrepancy was in no case so great as materially to influence the general character of the curve representing the variation in the value of the E.M.F. with varying currents, obtained on plotting the results by making the currents abscissæ and the electromotive forces ordinates. The following table (p. 53) exhibits, side by side, the values obtained in various acses selected as specimens: in numerous other cases not quoted, the curves obtained were considerably similar to those indicated by the figures given in the table and represented in fig. 2. The

Fig. 2.



resistance of the cell, R, is stated in ohms, and the electromotive forces in volts; the "maximum E.M.F." indicates the

* It might appear at first sight that a third valuation of the E.M.F. of the cell might be deduced as follows:—Since $e_1 = E_1 + 2{\cdot}5\,DR$, and also $e_2 = E_2 + 5{\cdot}0\,DR$, it results that $e_1 = e_2 = 2E_1 - E_2$; but it is evident that this value is such that e_1 is the arithmetical mean between e_2 and $2E_1 - E_2$, and hence that the average of the three values must be identical with e_1, and therefore less exact than the mean of e_1 and e_2.

		I.	II.	III.	IV.	V.	VI.	VII.
Zinc plates		Pure metal scraped bright.	Bright pure metal.	Commercial zinc plate scraped bright.	Coated over with a film of copper by immersion in weak copper-sulphate solution.	Pure metal amalgamated.	Pure metal amalgamated.	Pure metal amalgamated.
Copper plates		Freshly electro-covered.	Freshly electro-covered.	Freshly electro-covered.	Freshly electro-covered.	Electro-metal thoroughly amalgamated.	Freshly electro-covered.	Electro-metal thoroughly amalgamated.
Fluid surrounding zincs		Zinc-sulphate solution, sp. gr. 1·42.	Zinc-sulphate solution, sp. gr. 1·42.	Zinc-sulphate solution, sp. gr. 1·10.	Zinc-sulphate solution, sp. gr. 1·10.	Zinc-sulphate solution, sp. gr. 1·42.	Dilute sulphuric acid, sp. gr. 1·045.	Dilute sulphuric acid, sp. gr. 1·045.
R		11·2	13·0	9·5	5·4	11·15	4·11	4·2
Maximum E.M.F.		1·098	1·093	1·091	1·050	1·094	1·103	1·096
Current-density.		Observed amounts of Fall in Electromotive Force.						
C.G.S. units.	Microampères.							
·000001	10	...	...	·001	·001	...	0	...
·000002	20	...	...	·006	·006	...	·003	...
·000005	50	·009	·010	·013	·011	·005	·006	·008
·00001	100	·018	·021	·019	·018	·011	·009	·016
·00002	200	·025	·032	·028	·028	·023	·014	·028
·00005	500	·038	·049	·044	·046	·048	·027	·050
·0001	1000	·052	·069	·056	·060	·083	·041	·082
·0002	2000	·082	·101	·085	·087	·134	·063	·120
·0003	3000	·106	·130	·107	·110	·174	·084	·160
·0005	5000	·149	·179	·151	·155	·223	·125	·212
·0007	7000	...	...	...	...	...	·162	...

average value of the highest E.M.F. observed throughout the various series of readings, this value being always observed when either no current at all circulated, or a current of less magnitude than about 8 microampères* per square centimetre. The copper plates were uniformly surrounded by nearly saturated copper-sulphate solution (sp. gr. 1·175); the zinc plates were sometimes surrounded by nearly saturated zinc-sulphate solution (sp. gr. about 1·4), and were then lowest; in other cases they were highest, and were then surrounded either by zinc-sulphate solution of sp. gr. 1·10, or by dilute sulphuric acid of sp. gr. 1·045.

It is noticeable that whilst experiments Nos. I. and II. show that the curves obtained are by no means necessarily identical even when the conditions are sensibly the same (owing apparently to differences in the character of the copper deposited during the action of the cell), experiments Nos. I., III., and IV. indicate that but little difference in the curve is brought about by using commercial instead of pure zinc, or by altering the surface of the zinc by covering the bright metal with a film of copper (although more or less marked depressions in the maximum E.M.F. are occasioned thereby); on the other hand, experiments V. and VII., as compared with the others, indicate that amalgamating the copper renders the rate of fall in E.M.F. sensibly more rapid. But little difference, on the whole, is apparently occasioned in the curves by the use of zinc-sulphate solution (whether stronger or weaker than the copper-sulphate solution), as compared with dilute sulphuric acid; what difference is brought about is of this kind—that the sulphuric-acid curves slightly underlie the zinc-sulphate curves.

In none of the experiments made was any measurable depression of the E.M.F. of the cell brought about when the current flowed at a rate not exceeding 8 microampères per square centimetre; and in several cases this rate of flow might be doubled before any depression greater than ·001 volt (0·1

* In accordance with the nomenclature adopted by the recent International Electrical Congress, the term *ampère* is used throughout this paper to indicate what in the former paper of this series was designated a *weber*, viz. 0·1 C.G.S. current-unit; so that a microampère = ·0000001 C.G.S. current-unit $= 10^{-7}$ ampère.

per cent.) was occasioned. As a rule, when the current-density was from 30 to 50 microampères per square centimetre, a diminution in the E.M.F. of from 0·5 to 1 per cent. was brought about; whilst diminutions of 10 per cent. and upwards were occasioned when the current-density exceeded 3000. Supposing the same values to hold for ordinary Daniell cells (which is probably not quite the case, as the zinc and copper plates are usually unequal in size), it results that, with cells of ordinary dimensions (*e. g.* holding a litre and exposing a surface of 500 square centimetres), no appreciable diminution in the E.M.F. would be brought about when the current does not exceed $500 \times 8 = 4000$ microampères (·004 ampère); whilst diminutions of several tenths per cent. would be occasioned with currents of fivefold magnitude (·02 ampère), and diminutions of 10 per cent. and upwards when the current exceeds $500 \times 3000 = 1{,}500{,}000$ microampères (1·5 ampère).

Experiments made to determine the maximum Electromotive Forces of variously arranged Daniell Cells containing Zinc-sulphate solution around the zinc, and the maximum proportion of the Fall in the E.M.F. of the Cell with gradually increasing currents, that could be due to accumulation round the plates of fluids of different densities through the migrations of the ions.

106. A long series of experiments was next made with the object of determining how far the very considerable diminution in the E.M.F. of a Daniell cell, above shown to exist when moderately strong currents are generated, can be accounted for by the strengthening of the solution of zinc surrounding the plate, and the weakening of the copper-sulphate solution round the copper plate, which necessarily take place in consequence of the migration of the ions accompanying the passage of the current. Inasmuch as the use of dilute sulphuric acid introduces complications, these observations were made in the first instance with zinc-sulphate solutions only round the zinc plates; later on (§ 111), similar experiments with cells containing sulphuric acid are described.

It results from the experiments of Moser (*Annalen der Physik*, iii. p. 216) and H. F. Weber (Phil. Mag. [5] viii. pp. 487 &

523), that when a stronger solution of zinc (or copper) sulphate diffuses into a weaker one of the same salt, plates of zinc (or copper) placed in the two solutions acquire different potentials, that in the stronger solution being at the higher potential: the potential difference reckoned per a constant difference in specific gravity of solution (*e. g.* a difference of 0·1) is not constant, but depends on the actual values of the specific gravity, being less the stronger the solutions. The maximum value obtained (in the case of zinc-sulphate solutions containing respectively 60 and 1 per cent. of crystallized salt) was only ·036 Daniell, or about ·040 volt; whence it would seem that if the effect produced by zinc-sulphate solution in diffusing into copper-sulphate solution is of the same order of magnitude as that produced by diffusing into another zinc-sulphate solution of strength equivalent to that of the copper-sulphate solution, the effect on the E.M.F. of a Daniell cell, due to migration of the ions, cannot possibly materially exceed ·04 volt; whilst, whatever the magnitude of the effect, it must tend to diminish the E.M.F. of the cell, since it partially equalizes the difference of potential between the zinc and copper plates set up by the chemical action alone. In order to find out the actual magnitude of the diminution due to this diffusive action in various cases, a number of determinations were first made of the E.M.F. set up in various forms of Daniell cell when generating currents of magnitude not exceeding 8 microampères per square centimetre (and usually when generating no current at all), *the zinc- and copper-sulphate solutions being in any given case of the same specific gravity**. The average values being thus fixed, the observations were then repeated, using solutions not of the same specific gravity. It is particularly noteworthy in this connexion, that the E.M.F.

* Although two solutions of zinc and copper sulphate, respectively of the same specific gravity, are not absolutely chemically equivalent to one another (*i. e.* do not contain precisely equivalent percentages of the two salts), yet the difference in specific gravity between any two solutions of equivalent strengths is so small that, for all practical purposes, it may be assumed that when the specific gravity is the same the solutions are of equivalent strengths. Direct determinations of the specific gravities of various solutions of equivalent strengths (made by dissolving known weights of the air-dry pure salts to known weights of aqueous solutions), gave the following results:—

of a Daniell cell was found to be *sensibly independent of the strength of the solutions when both are of the same specific gravity*—*i. e.* the deviations observed from equality were less than the experimental errors.

The cells employed were constructed of two small beakers —one containing zinc-sulphate solution and plates of zinc (scraped bright, covered with electro-deposited metal, or amalgamated with pure mercury), and the other copper-sulphate solution and similar copper plates. The two beakers were connected, in the way described by Raoult (*Ann. de Chim. et de Phys.* 4th series, ii. p. 317, and iv. p. 392), by means of an inverted Y-tube, the ends of which, dipping into the two beakers respectively, were covered over with thin bladder, the tube being filled with the zinc-sulphate solution. Each one of the zinc and copper plates used was soldered to a platinum wire fused into a piece of glass tubing, forming a mercury-cup; the soldering and the whole length of the platinum wire being thickly covered with gutta percha, so that only zinc (or copper) was exposed to the fluid. The plates were then connected with a series of mercury-cups in such a way that, by simply moving a double switch connected at one end with two mercury-cups in connexion with the electrometer-quadrants, and dipping at the other end into two of the series of cups, any required pair of zinc and copper plates could be brought

Percentage of $CuSO_4, 5H_2O$.	Specific gravity at 18°.	Equivalent percentage of $ZnSO_4, 7H_2O$.	Specific gravity at 18°.
1	1·006	1·15	1·007
3·75	1·023	4·3	1·026
7·5	1·047	8·6	1·053
15	1·098	17·2	1·107
22·5	1·156	25·9	1·163
30	1·214	34·5	1·223

The 30-per-cent. solution of copper sulphate was slightly supersaturated, and deposited crystals on standing in a closed vessel; saturated zinc-sulphate solution has a specific gravity upwards of 1·4. It is noteworthy that these figures indicate that when given bulks of water and of either zinc- or copper-sulphate solution are mixed, an *increase* in bulk occurs, thus agreeing with J. Thomsen's result that dilution of a solution of either salt is accompanied by heat-absorption (§ 113).

into connexion with the electrometer. Fig. 3 shows the arrangement used for two pairs of plates, and fig. 4 that for

Fig. 3.

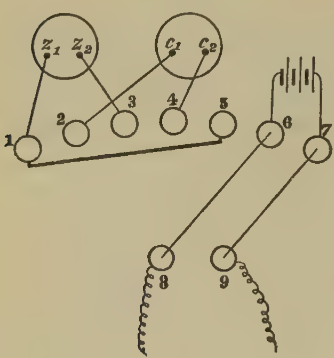
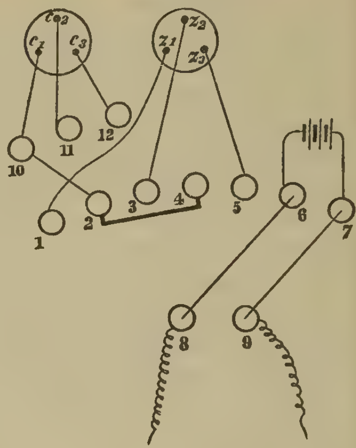


Fig. 4.



three pairs. In the former the two zinc plates, z_1 and z_2, are connected with mercury-cups Nos. 1 and 3 (No. 1 being also connected with No. 5), whilst the two copper plates, c_1 and c_2, are connected with cups Nos. 2 and 4 respectively. Cups Nos. 6 and 7 are connected with a standard cell (the error of which, in reference to the average taken as 1·457 volt, is known). By means of a double switch any pair of the series of cups 1 to 7 can be connected with cups 8 and 9, which are connected with the electrometer through the usual reversing-gear; so that when Nos. 1 and 2, 2 and 3, 3 and 4, and 4 and 5 are thus connected, the electromotive forces due to the combinations z_1c_1, c_1z_2, z_2c_2, c_2z_1 are respectively read off; whilst when 6 and 7 are connected (as represented in the figure) the electrometer-scale is standardized. In actually taking readings a double set was always employed, the switch being successively used to connect the four combinations and the standard with the electrometer, and then to connect them again in reversed order; so that, by taking the averages of the two sets, any error due to running down of the electrometer during the readings might be eliminated (in practice the running down during the period was insensible, the variation being usually at most only 2 or 3 per cent. during the whole

day, and often much less). When three pairs of plates were used, the three zincs were connected respectively with cups 1, 3, and 5; whilst cup No. 2 was connected with No. 4, and also, by means of a movable wire, with either of three other cups, Nos. 10, 11, and 12, with which respectively the three copper plates were connected: so that when No. 2 was connected with 10, as represented in the figure, the combinations c_1z_1, c_1z_2, and c_1z_3 could be read off by connecting the double switch with 1 and 2, 2 and 3 (or 3 and 4), and 4 and 5 successively; and similarly for the other combinations.

107. The ultimate results of upwards of a hundred series of valuations of the electromotive forces of various combinations, mostly lasting over four hours, were as follows:—

(1) With the stronger solutions used (specific gravities 1·100 to 1·175) the E.M.F. set up after the first few minutes remained sensibly constant for several hours (the temperature being constant), never differing from the final average of the four average sets of readings made in each of the first four hours by amounts outside the limits of observational error. For instance, the following values were obtained in one experiment, in which the temperature throughout was close to 18°, the specific gravity of the solutions being 1·175:—

Combination.	Average E.M.F. determined during the				Final average.
	1st hour.	2nd hour.	3rd hour.	4th hour.	
Amalgamated zinc—electro-copper ...	1·112	1·113	1·114	1·114	1·1132
Bright zinc—electro-copper	1·110	1·109	1·112	1·110	1·1102
Amalgamated zinc—bright copper ...	1·119	1·122	1·122	1·120	1·1207
Bright zinc—bright copper	1·117	1·115	1·118	1·118	1·1170

Very similar results were obtained in all the other cases. After twenty-four hours the E.M.F. usually diminished to a greater or less extent. These changes are referred to later on (§ 108), being probably due to oxidation of the metals by dissolved air.

(2) With weaker solutions (sp. gr. 1·0065 to 1·050) the E.M.F developed during the first half hour or so was usually

slightly lower than the value attained subsequently; which value remained sensibly constant for several hours, and then fell to a greater or lesser extent, as with the stronger solutions. Accordingly, in such cases the lower readings during the first half hour or so were not taken into account in the final average. For any given combination of plates, the final average thus obtained with weaker solutions was sensibly identical with that obtained with the stronger solutions*.

(3) The combinations that gave the most constant results on repetition of the experiments were those containing amalgamated zinc and either electro-copper or amalgamated copper; next to which were those with electro-deposited zinc and these same kinds of copper plates. Combinations containing either bright zinc or bright copper (*i. e.* rods of fused metal or sheets of rolled metal filed, scraped, or sand-papered to

* The conclusion that the E.M.F. developed by a given pair of plates immersed, the one in zinc-sulphate, the other in copper-sulphate solution, is sensibly independent of the strength of the solutions when both are of the same density (or, at least, that the variation in E.M.F. caused by variation in strength of the solutions is not outside the limits of experimental error), is further corroborated by the results of still more direct experiments on the matter. Three cells were arranged, containing solutions respectively of the specific gravities 1·010, 1·090, and 1·175, each containing a recently electro-coppered plate and a freshly amalgamated zinc plate. A number of readings were taken of the potential-differences subsisting between the plates in each case; and then the plates were exchanged—the pair from the first cell being placed in the second, that originally in the second being transferred to the third, and so on. After a new set of readings had been taken, the plates were again exchanged and a third set of readings taken; so that each pair of plates was read in each cell. The following figures were finally obtained, all readings taken during the first half hours after immersion of the plates being rejected:—

Specific gravity 1·010.		Specific gravity 1·090.		Specific gravity 1·175.	
1st pair of plates	1·1127	2nd pair of plates	1·1122	3rd pair of plates	1·1125
2nd " "	1·1130	3rd " "	1·1115	1st " "	1·1118
3rd " "	1·1140	1st " "	1·1135	2nd " "	1·1133
Mean	1·1132	Mean	1·1124	Mean	1·1125

In each case the value found as the mean for the three pairs of plates differs from the general average 1·1127 by an amount so small as hardly, if at all, to be outside the limits of experimental error.

perfect brightness) exhibited a considerably wider range of variation. By comparing various bright copper plates with one and the same amalgamated zinc plate, or various bright zinc plates with one and the same electro-copper plate, it was found that differences, amounting nearly to 0·010 volt in the most extreme instances, were observable in each case with different bright plates as compared with one another. On the other hand, on comparing various electro-copper or amalgamated copper plates with one and the same zinc plate, or various amalgamated zinc plates with one and the same copper plate, the extreme ranges of fluctuation were found to be not more than half those observed with bright plates, and usually did not exceed $\pm$·001 as compared with the average.

(4) As the ultimate average result of all the determinations made, it was found that an amalgamated zinc plate gave, when opposed to a given copper plate, an E.M.F. lower by ·002 volt than a bright zinc plate, and lower by ·001 volt than an electro-zinc plate. The actual differences in various experiments ranged in the former case between +·006 and −·004, the bright zinc plate sometimes giving a higher value, and sometimes a lower value, than the amalgamated plate—more frequently the former. (In the example quoted above, the bright zinc plate gave a value lower by ·0030 when opposed to an electro-copper plate, and by ·0037 when opposed to a bright copper plate.) With electro-zinc as compared with amalgamated zinc, the difference ranged between +·004 and −·003, the electro-zinc sometimes giving a higher and sometimes a lower value than the amalgamated zinc, more usually the former.

(5) Similarly, the effect of substituting a bright copper plate for an electro one in any given combination was uniformly to cause an increase in the E.M.F. by an amount varying between ·001 and ·010 volt, and averaging, on the whole, ·006. (In the example quoted above, bright copper gives a higher value than electro-copper by ·0075 when opposed to amalgamated zinc, and by ·0068 when opposed to bright zinc.) The effect of amalgamating a copper plate was found to be, on the whole, to give an E.M.F. lower by ·001 than that given under the same conditions by a freshly electro-coppered plate, the actual difference ranging between +·002 and −·003, the amalga-

mated plate sometimes giving a higher value and sometimes a lower one than the electro-plate, more frequently the latter. It is worthy of notice that no sensible difference was observable whether the plate amalgamated were previously of bright rolled metal or of electro-metal; so that, on the whole, the effect of amalgamating a bright rolled plate was to depress the E.M.F. by ·006+·001=·007.

(6) The average results of all the experiments made are contained in the following tabular statement: increase in E.M.F. is indicated by the + sign, and diminution by the − sign:—

Variation in the E.M.F. due to the use of zinc- and copper-sulphate solutions of different strengths between the limits of sp. gr. 1·0065 and 1·175, both solutions being of the same specific gravity in any given case . . .	Less than ±·001.

	Maximum.	Minimum.	Range.	Average.
Effect of substituting for fresh electro-copper:—				
Bright rolled copper sheet	+·010	+·001	·009	+·006
Amalgamated copper (surface wet with fluid mercury)	+·002	−·003	·005	−·001
Effect of substituting for fresh electro-zinc:—				
Bright cast zinc	+·005	−·005	·010	+·001
Amalgamated zinc (surface wet with fluid mercury)	+·003	−·004	·007	−·001
Electromotive force of combinations:—				
Amalgamated zinc—Amalgamated copper	1·115	1·110	·005	1·113
,, ,, Electro-copper	1·116	1·111	·005	1·114
,, ,, Bright copper	1·124	1·115	·009	1·120
Electro-zinc—Amalgamated copper	1·116	1·110	·006	1·114
,, ,, Electro-copper	1·118	1·111	·007	1·115
,, ,, Bright copper	1·124	1·114	·010	1·121
Bright zinc—Amalgamated copper	1·119	1·109	·010	1·115
,, ,, Electro-copper	1·121	1·110	·011	1·116
,, ,, Bright copper	1·126	1·112	·014	1·122

108. The above figures are, as already stated, derived from the observations made during the first four hours after setting up the cells, the values registered during the first half hour or so with weaker solutions being rejected on account of their frequently being lower than the sensibly constant values attained to

subsequently. When the cells were allowed to stand for twenty-four hours, or for longer periods, a greater or less fall in the E.M.F. was usually noticed: by taking out any pair of the plates (*e. g.* the amalgamated zinc and the electro-copper plates) and replacing them by a freshly prepared similar pair, it was found that the value rose again to sensibly the same value as on the previous day when only set up a few hours; so that by taking out first one and then the other of the pair of plates, determinations could be made of the amount of the total fall attributable to alterations of either plate separately. The actual values thus obtained fluctuated considerably. As a general rule, it was found that bright copper plates gave the same value after twenty-four hours' immersion as they did at first; but occasionally the value was lowered by ·002 to ·004. Electro-copper plates usually gave values less by ·002 or ·003 after twenty-four hours than at first; and in some instances, when the pink electro-metal was sensibly browned or discoloured by oxidation, either all over or here and there in spots, the diminution was even greater, sometimes as much as ·010. Amalgamated copper plates, if the surface were still white and brilliant after twenty-four hours, gave the same value as at first; but if the mercury had sunk into the copper, and brown spots of oxidized metal were here and there visible, the E.M.F. was a few thousandths of a volt lower than at first. With the zinc plates greater diminutions were, as a rule, observed. In some cases amalgamated plates showed little or no diminution after twenty-four hours; but generally a diminution of ·002 to ·005 was observed; whilst with bright and electro-zinc plates diminutions of from ·001 to ·015 were noticed. On the whole, after twenty-four hours the E.M.F. was sometimes unchanged, and sometimes less by ·020. After forty-eight hours the fall was more perceptible still, the few combinations that had not appreciably altered during twenty-four hours always showing a decided fall after a longer period. It is noticeable in this connexion, that cells after Daniell's construction, but containing other metals than copper, did not always give the same results as normal Daniell cells. Thus, for instance, whilst cells containing cadmium sulphate and cadmium plates behaved like copper Daniells, in that the E.M.F. was sensibly steady for some hours after first setting up, and only exhibited a mea-

surable fall after several hours had elapsed, and not always then, analogous cells containing silver sulphate and silver plates invariably showed a perceptible fall in less than an hour after first setting up, the diminution becoming progressively greater as a longer time elapsed. That this diminution was due to a change (presumably oxidation by dissolved air) induced on the surface of the zinc plate was rendered evident by the fact that, on taking out from such a zinc-silver cell the zinc plate after the lapse of an hour or more, and opposing it to electro-copper in an ordinary zinc-copper Daniell, an E.M.F. was indicated considerably less than the value given by a fresh zinc plate, and usually just about as much less as represented the fall in E.M.F. observed with the zinc-silver cell at the end of the period during which it was observed, as compared with the E.M.F. at the beginning of that period, when it was newly set up.

109. It is further to be noticed, that all the above-mentioned figures were obtained with cells the nature of the construction of which was such that diffusion of copper-sulphate into the zinc-sulphate solution, and consequent deposition of copper on the surface of the zinc, *did not take place at all* during the whole time that the observations lasted. With ordinary gravity-cells it is almost impracticable to prevent traces of copper reaching the zinc after some twenty-four hours at latest: the effect of the deposition of even the faintest traces of copper on the zinc surface is to cause a considerable fraction of the energy due to the solution of the zinc to become non-adjuvant, and thus materially to diminish the E.M.F. Thus, for instance, the following figures were obtained with one cell, and similar ones in numerous other cases:—

E.M.F. of gravity-cell newly set up: zinc plate wholly free from copper	1·103
After 8 hours: faint tarnish visible on the zinc .	1·095
„ 24 hours: slight film of copper on the zinc .	1·070
„ 48 hours: thick film of copper on the zinc .	1·045

In much the same way, the presence of even small quantities of impurities in the zinc causes an appreciable diminution in the E.M.F. In all the above-described observations, some of the purest zinc that could be bought was employed, being

fashioned into plates and rods by melting in a porcelain crucible, pouring out on a fire-clay tile, and cutting into slips with a chisel, &c. When commercial sheet or cast zinc was used, or when pure zinc was amalgamated with imperfectly purified mercury, the E.M.F. developed when such zinc was opposed to a given copper plate was often very materially less than the value obtained with pure zinc, or pure zinc and pure mercury. Thus, whilst values varying between 1·111 and 1·116 were obtained with pure amalgamated zinc opposed to fresh electro-copper as above described, values varying from 1·080 to 1·109 were obtained with commercial zinc amalgamated with pure mercury, and with pure zinc amalgamated with impure mercury, similarly opposed.

It is abundantly evident from the above-described results (not to speak of those detailed later on), that "the E.M.F. of a Daniell cell" is a unit of comparison subject to decidedly wide limits of fluctuation; but that it is possible to reproduce a standard cell of the kind within a maximum limit of variation of about $\pm 0{\cdot}25$ per. cent., by using Raoult's form of construction together with a recently electro-coppered or amalgamated copper plate, and a pure zinc plate amalgamated with pure mercury, the zinc- and copper-sulphate solutions used being both of the same specific gravity, the precise value of the specific gravity being immaterial. Even when made, however, such a standard cell cannot be relied on for more than a few hours. It will be shown in a subsequent paper that whilst Latimer Clark's mercurous-sulphate cell is subject to an even wider range of fluctuation in E.M.F. than the best forms of Daniell cell, its permanence is very far superior, a well-constructed cell giving absolutely the same value (when used in conjunction with a quadrant electrometer only) for months and months together.

110. The above described experiments having given results indicating the average values of the electromotive forces developed with different characters of plates when the specific gravities of the solutions surrounding the plates are the same, further series of observations were made with cells in which the zinc- and copper-sulphate solutions were not of the same

specific gravity, the mode of operating being otherwise the same as before. As predicable from Moser's figures, and as previously observed by H. F. Weber, it was found that when the copper-sulphate solution was the more dense of the two, the E.M.F. was higher than with solutions of equal density, and *vice versâ* when the zinc-sulphate solution was the stronger. The average results of various observations, mostly lasting over four hours as before, are contained in the following table; in every case the zinc plate employed was of pure metal and amalgamated with pure mercury.

Effect of increasing the strength of the Zinc-sulphate solution relatively to that of the Copper-sulphate.

Specific gravity of solution used.		Nature of copper plate.	Average E.M.F. at 18° of combination.			Ratio of difference in E.M.F. to difference in specific gravity.
Zinc sulphate.	Copper sulphate.		Observed.	Previously found for solutions of equal specific gravity.	Difference.	
1·145	1·010	Electro.	1·099	1·114	·015	
		Bright.	1·107	1·120	·013	
					·014	$\frac{·014}{·135}$ = ·105
1·175	1·050	Electro.	1·102	1·114	·012	
		Bright.	1·108	1·120	·012	
					·012	$\frac{·012}{·125}$ = ·096
1·260	1·050	Electro.	1·096	1·114	·018	
		Bright.	1·103	1·120	·017	
					·0175	$\frac{·0175}{·021}$ = ·083
*1·395	1·010	Electro.	1·077	1·114	·037	
		Bright.	1·086	1·120	·034	
					·0355	$\frac{·0355}{·0385}$ = ·092
*1·395	*1·175	Electro.	1·097	1·114	·017	
		Bright.	1·104	1·120	·016	
					·0165	·22 = ·075

Effect of increasing the strength of the Copper-sulphate solution relatively to that of the Zinc-sulphate.

1·010	1·090	Electro.	1·129	1·114	·015	
		Bright.	1·135	1·120	·015	
					·015	$\frac{\cdot 01}{\cdot 080}=0\cdot 188$
1·010	*1·175	Electro.	1·132	1·114	·018	
		Bright.	1·141	1·120	·021	
					·0195	$\frac{\cdot 0195}{\cdot 165}=\cdot 118$
1·050	*1·175	Electro.	1·126	1·114	·012	
		Bright.	1·133	1·120	·013	
					·0125	$\frac{\cdot 0125}{\cdot 125}=\cdot 100$
1·090	*1·175	Electro.	1·123	1·114	·009	
		Bright.	1·128	1·120	·008	
					·0085	$\frac{\cdot 0085}{\cdot 0085}=\cdot 100$

It is evident from these figures that the accumulation round the zinc plate of zinc sulphate, and the exhaustion of the copper sulphate in the solution round the copper plate, even if carried out to the utmost possible extent, could not diminish the E.M.F. of a Daniell cell by more than ·03 to ·04 volt; whilst it is hardly probable, even with tolerably rapid currents, that the accumulation would suffice to diminish the E.M.F. by more than half that amount—a diminution almost negligible in comparison with the much larger amounts, 0·1 volt and upwards, found above to be due to this cause of diminution and non-adjuvancy jointly.

It is noticeable in passing that the above figures show that when two solutions of zinc and copper sulphates interdiffuse, the E.M.F. set up (like that produced by the interdiffusion of two zinc-sulphate, or of two copper-sulphate solutions, as studied by Moser) is of such a character that the stronger solution acquires the higher potential; the actual value of the E.M.F. developed also *is less for a given difference in specific gravity the stronger the solutions*, and, so far as the two sets of results can be compared, agrees fairly with the values deducible from Moser's experiments—indicating that the difference between the E.M.F. set up when two different solutions of $\left\{\begin{array}{l}\text{zinc}\\\text{copper}\end{array}\right.$

* Solution almost saturated at ordinary temperatures.

sulphate diffuse into a constant $\left.\begin{matrix}\text{copper}\\\text{zinc}\end{matrix}\right\}$ sulphate solution is substantially the same as the E.M.F. set up when these two different $\left.\begin{matrix}\text{zinc}\\\text{copper}\end{matrix}\right\}$ sulphate solutions diffuse into each other. Moreover the effect of a given alteration in the strength of the zinc-sulphate solution (every thing else remaining the same) is sensibly equal in amount, but opposite in sign, to that of a similar alteration in the strength of the copper-sulphate solution; it is evident that only when this is the case can the E.M.F. of the cell be the same whether the solutions be strong or weak. It will be shown in a future paper that this property, though not absolutely peculiar to the normal Daniell cell, is still rather the exception than the rule with analogous voltaic combinations.

Experiments with Daniell Cells containing dilute Sulphuric Acid.

111. In all the above described experiments, the solution surrounding the zinc plate was one of pure zinc sulphate. Various previous experimenters, notably H. F. Weber, have found higher values for the electromotive forces of Daniell cells containing dilute sulphuric acid than for those containing zinc-sulphate solution (*vide* § 113): *à priori* a higher value might be anticipated, because a notable amount of heat is evolved on further diluting even weak sulphuric acid; so that the total energy gained in the cell is not merely that due to the displacement of copper from copper sulphate by zinc, but also that gained in the dilution of the sulphuric acid through the diffusion which necessarily goes on. On trying experiments of the same kind as those just described with cells containing dilute sulphuric acid of various strengths (the zinc being amalgamated), it was found that not only was there a considerable want of permanence in the E.M.F. set up, the values perceptibly decreasing after a period of time (varying in different cases from half an hour to several hours) had elapsed since setting up the cells, but, further, that two cells, apparently set up in identically the same way, exhibited much greater differences in their readings during the period before the E.M.F. began to diminish, than were observed in the zinc-sulphate cells examined as above described. On the whole,

however, the average values obtained distinctly pointed to the conclusion that, when the acid and copper-sulphate solutions are of the same specific gravity, the E.M.F. rises with strength of the solution; and that when they are not of the same specific gravity (the acid not being stronger than specific gravity 1·18), the E.M.F. is sensibly that due to a cell containing liquids both of specific gravity equal to that of the acid in the cell examined, corrected by the addition (or subtraction) of a quantity representing the difference in specific gravity of the solutions multiplied by the numerical value deduced from the zinc-sulphate cell experiments, representing the difference in E.M.F. produced by a variation in the specific gravity of the copper-sulphate solutions equal to that between the acid and copper sulphate in the cell examined: *i. e*, if, for example, the E.M.F. of a cell containing both liquids of sp. gr. 1·100 be E, that of a copper-cell containing acid of sp. gr. 1·100 and copper-sulphate solution of sp. gr. 1·010 will be $E-(1{\cdot}100-1{\cdot}010)\times\alpha$, where α is the factor expressing the diminution per unit difference of specific gravity in the E.M.F. between the limits of sp. gr. 1·010 and 1·100 for copper-sulphate solution. Similarly, that of a cell containing acid of sp. gr. 1·100 and copper-sulphate solution of sp. gr. 1·175 would be $E+(1{\cdot}175-1{\cdot}100)\beta$, where β is the corresponding factor for a difference in specific gravity between the limits 1·100 and 1·175.

Thus, for instance, the following values were obtained with a cell containing fluids both of sp. gr. 1·175, the temperature being close to 18° throughout.

Period since setting up.	During 1st hour.	2nd hour.	3rd hour.	4th hour.	Average.
Electro-copper plate	1·161	1·162	1·163	1·160	1·1615
Bright " "	1·167	1·168	1·168	1·166	1·1672

In most cases, however, a distinct fall of upwards of ·005 volt occurred in less than four hours.

A number of similar series of observations (upwards of thirty) with various other cells, in which the fluids were always of equal specific gravity, gave the following results, the observations being only continued as long as the E.M.F.

remained sensibly constant—*i. e.* for a period of time varying from thirty minutes to four hours, and averaging about two hours. In all these experiments electro-copper and amalgamated pure zinc plates were employed.

Specific gravity of fluids.	Electromotive force set up, in volts.		
	Maximum.	Minimum.	Average.
1·010	1·143	1·121	1·129
1·050	1·150	1·128	1·139
1·090	1·155	1·137	1·148
1·175	1·179	1·161	1·169

Evidently, even with the weakest acid, the E.M.F. is sensibly above that developed with zinc-sulphate cells—viz. 1·114; whilst with stronger solutions the difference is yet more marked.

112. A number of analogous observations were made with cells containing dilute sulphuric-acid and copper-sulphate solutions, not both of the same specific gravity: the average results were as follows:—

Specific gravity of solutions.		Excess of specific gravity of copper sulphate over acid solution.	Approximate correction for excess of specific gravity of copper sulphate.	Average E.M.F. observed.	Observed E.M.F. corrected for excess of specific gravity of copper sulphate.
Acid.	Copper sulphate.				
1·010	1·050	+·040	−0·008	1·147	1·139
1·010	1·090	+·080	−0·015	1·135	1·120
1·010	1·175	+·165	−0·019	1·137	1·118
				Average......	= 1·126
1·050	1·175	+·125	−0·012	1·148	1·136
1·175	1·050	−·125	+0·012	1·168	1·180
1·175	1·090	−·085	+0·008	1·164	1·170
				Average......	= 1·175

The final averages representing the E.M.F. corrected to the uniform specific gravities 1·010, 1·050, and 1·175 respectively, do not differ from the values directly obtained as just described for these specific gravities by amounts outside the limits of experimental error in this class of the various experiments made.

A peculiar result was obtained with cells containing sulphuric acid of sp. gr. 1·265, and nearly saturated copper-sulphate solution of sp. gr. 1·175. The E.M.F. was considerably depreciated, the average value in four sets of experiments with electro-copper and amalgamated pure zinc plates being only 1·084 (maximum 1·095, minimum 1·067). On standing a few hours, copper-sulphate crystals formed at the junction of the two fluids, showing a much less degree of solubility of the salt in the acid fluid formed than in pure water.

Relationships between the maximum E.M.F. developed by a Daniell Cell and the Energy due to the net Chemical action taking place therein.

113. The above-described results afford a ready explanation of the discrepancies between the valuations of the E.M.F. of a Daniell cell that have been made in absolute measure by various observers, amongst the more important of which may be cited those of Bosscha (Pogg. *Ann.* ci. p. 517, 1856), von Waltenhofen (Pogg. *Ann.* cxxxiii. p. 478, 1868), Kohlrausch (Pogg. *Ann.* cxli. p. 456, and *Ergänz.* vi. p. 35), H.F. Weber (Phil. Mag. 1878, [5] v. p. 189), and J. Thomsen (Wied. *Ann.* xi. p. 246, 1880), all of which valuations lie between 1·088 and 1·132 volt when reduced to that unit (and, in the case of Bosscha's results, corrected for an error of about 8 per cent. in the value of the coil used by him). To these may be further added the electrostatic valuations of Sir W. Thomson and Latimer Clark, both of which lie near to 1·11 volt. Favre (*Comptes Rendus*, lxix. p. 35) and Raoult (*Ann. Chem. Phys.* [4] ii. p. 338, and iv. p. 392) obtained by methods involving calorimetric measurements numbers representing the "galvanic heat" of a Daniell cell, and equivalent to considerably smaller electromotive forces, their valuations (23993 and 23900 gramme-degrees respectively) corresponding to 1·058 and 1·054 volt. In these instances, and in the case of the lower values obtained by other observers, doubtless the "polarizations" produced by the passage of the tolerably powerful currents employed were considerable. The highest values were obtained with cells in which dilute sulphuric acid was used; thus, H. F. Weber found that a perceptibly higher value was obtained with such a cell than with one containing zinc-sulphate solution, viz. 1·1317 and 1·1286 (mean = 1·1301)

as compared with 1·0954. That this should be the case is predicable from the nature of the heat-evolutions taking place when zinc is dissolved in acid of various strengths. Let an amount of heat, H_1, be evolved when a gramme-equivalent of zinc oxide is dissolved in sulphuric acid of given strength, SO_4H_2, m H_2O; and let H_2 be the heat evolved on its solution in acid of a different strength $SO_4 H_2$, n $H_2 O$, n being less than m. Let the solution SO_4Zn, nH_2O, resulting in this latter case, evolve h_1 of heat on the addition of $(m-n)$ H_2O, so as to form the solution $SO_4 Zn$, m H_2O; and let the heat evolved on the addition of this quantity of water to SO_4H_2, n $H_2 O$, so as to convert it into $SO_4 H_2$, m H_2O, be h_2. Then, if the zinc oxide were dissolved in the stronger acid, and the zinc sulphate diluted, the heat-evolution would be H_2+h_1; whilst if the acid were diluted first, and the zinc oxide were then dissolved in it, the total heat evolved would be H_1+h_2. Since of necessity the two amounts of heat, H_2+h_1 and H_1+h_2, must be equal, it results that $H_2=H_1-h_1+h_2$. Now h_2 is a considerable positive quantity in all cases; whilst Thomsen's results on the heat evolved on solution of salts in water (*Deut. chem. Ges. Berichte*, 1873, p. 710) indicate that when the solution is accompanied by heat-absorption (as is the case with zinc sulphate), a further heat-absorption takes place on diluting a stronger solution of the salt with water, so that h_1 has a negative value. Hence, on both accounts, H_2 is greater than H_1; that is, the work gained in the synthesis ZnO, SO_3 x aq. increases as x diminishes. Since the net chemical action in a Daniell cell is equivalent to the result of the actions $(Zn, O)+(ZnO, SO_3\ x\ aq.)-(Cu, O, SO_3\ y\ aq.)$, it finally results that the chemical action taking place in the cell develops an amount of energy which increases, *cæteris paribus*, as x diminishes, *i. e.* is greater the more concentrated the acid surrounding the zinc.

On the other hand, when the zinc plate is surrounded by zinc-sulphate solution instead of sulphuric acid, the effect of variation in the strengths of the copper- and zinc-sulphate solutions will be comparatively but small when both are of the same degree of molecular concentration (which, as shown above, is very nearly the case when they are of the same density). If $SO_4 Zn$, nH_2O evolves, as before, h_1 on addi-

tion of $(m-n)H_2O$, and $SO_4 Cu, nH_2O$ evolves h_3 on a similar addition, and if H_3 and H_4 are respectively the heats evolved when zinc displaces copper from $Cu SO_4, nH_2O$, and $Cu SO_4, mH_2O$, it results that, if zinc displace copper from the stronger solution and the resulting $SO_4 Zn, nH_2O$ be diluted to $Zn SO_4, mH_2O$, the heat evolved will be H_3+h_1; whilst if the copper-sulphate solution be first diluted and then the zinc displaces the copper, the heat-evolution is H_4+h_3. Since, of necessity, $H_3+h_1=H_4+h_3$, it follows that $H_3=H_4+h_3-h_1$. Now, since the solution of zinc and copper sulphates (crystallized) is in each case accompanied by heat-absorption, it results that h_3 and h_1 are both negative, and hence that h_3-h_1 is negligible if h_3 is any thing like comparable with h_1 in magnitude; so that in this case the energy developed by the net chemical action taking place in a Daniell cell must be practically independent of the degree of concentration of the solutions.

114. The earlier calculations of J. Thomsen, referred to in §16, as to the heat evolved in the displacement of copper from copper sulphate by zinc, are for various reasons probably less accurate than the later results obtained by him (*Journ. prak. Chem.* [2] xi. p. 412, and xii. p. 271); these different values may be thus contrasted, the values being gramme-degrees per gramme-molecule:—

	Values from experiments by Andrews, Dulong, Hess, Favre and Silbermann, and J. Thomsen.	Values from later experiments of J. Thomsen.
Zn, O, SO_3 aq. =	108460	106090
Cu, O, SO_3 aq. =	56216	55960
Difference =	52244	50130
Corresponding in volts (per gramme-equivalent) to	1·152	.... 1·105

The earlier value is deduced from observations in which the heat of formation of copper oxide from the metal by combustion is involved, the copper being in a more or less *compact* state, filings &c.; the latter involves the determination of the heat-evolution during the precipitation of *spongy* copper from copper sulphate by iron. Leaving out of sight other sources of difference between the two values, this affords a reason why the former value should be the higher, since heat is evolved in the transformation of spongy into compact

copper *. On the whole, it is evident that the net chemical change taking place in a Daniell cell (*i. e.* the displacement of copper from copper sulphate by zinc) corresponds to an E.M.F. which is a little higher than 1·105 volt by an amount which is the greater the more compact the copper precipitated, and is approximately constant when the zinc plate is surrounded by zinc-sulphate solution of the same equivalent strength as the copper-sulphate solution surrounding the copper plate, but is influenced by the strength of the dilute sulphuric acid when the fluid surrounds the zinc plate. The amount of this influence can be approximately calculated from Thomsen's determinations of the heat developed in the formation of the solutions of strengths indicated by H_2SO_4, nH_2O where n varies (*Deut. chem. Ges. Berichte*, iii. p. 496). Thomsen finds in gramme-degrees per gramme molecule :—

n	gramme-degrees.	n	gramme-degrees.
9	14940	199	17056
19	16248	399	17304
49	16676	799	17632
99	16850	1599	17848

From which table the values for any intermediate values of n can be obtained by interpolation. In the experiments leading to the valuatiou 50130 gramme-degrees for the heat developed during the precipitation of a gramme molecule of copper by zinc, Thomsen used fluids containing altogether 800 molecules of water to one of zinc sulphate, &c. Hence, were the acid used in the synthesis Zn, O, SO_3 aq., to be $H_2 SO_4$,

* That this is so is shown by the circumstance that if a current be sent through a decomposing-cell containing copper-sulphate solution and copper electrodes, of which the positive one is of compact rolled metal, a considerably higher difference of potential is set up, under any given conditions and with a steady current, than is set up when the + electrode is replaced by one covered with freshly electro-deposited metal. The more spongy texture of the latter corresponds to a greater heat-development during solution than that taking place with the compact metal, and hence to a diminution of the work that has to be done by the current in passing; with not very powerful currents the difference often exceeds ·02 or ·03 volt, corresponding to 450 to 700 gramme-degrees per gramme equivalent. In a somewhat similar way, but using the mercurial calorimeter, Favre found (*Comptes Rendus*, lxxiii. p. 1258) that electro-copper gave out about 1000 gramme-degrees more heat than rolled metal per gramme equivalent; this would correspond to an E.M.F. of ·044 volt.

17 H_2O (corresponding nearly to the sp. gr. 1·175), instead of $H_2 SO_4$, 800 H_2O, the heat-development would be greater than 106090 by 17632−15986=1646 gramme-degrees per gramme molecule (15986 being the heat of dilution of sulphuric acid when $n=17$, deduced from the above table): this corresponds to 823 gramme-degrees per gramme equivalent =·036 volt; *i. e.* the E.M.F. corresponding to the heat-development during the displacement of copper from copper sulphate by zinc would be greater than 1·105 volt by ·036, or would be 1·141 volt. To this amount should also be added the value of the E.M.F. equivalent to the heat-absorption during the dilution of Zn SO_4, 17 H_2O to Zn SO_4, 800 H_2O. In a similar fashion it is calculable that to the value 1·105 should be added the amounts ·023, ·019, and ·008 volt when sulphuric acid of sp. gr. 1·090, 1·050, and 1·010 respectively surrounds the zinc, giving the sums 1·128, 1·124, and 1·113 respectively. Hence, finally, the following tables of values result:—

Zinc surrounded by Zinc-sulphate solution.

Electromotive force corresponding to net chemical action.	Electromotive force observed.	
$1·105+x$, where x is a small quantity varying with the physical condition of the copper deposited.	Bright zinc opposed to bright copper	1·122
	Bright zinc opposed to electro-copper	1·116
	Bright zinc opposed to amalgamated copper . . .	1·115
	Amalgamated zinc opposed to bright copper	1·120
	Amalgamated zinc opposed to electro-copper	1·114
	Amalgamated zinc opposed to amalgamated copper . .	1·113
	Electro-zinc opposed to bright copper	1·121
	Electro-zinc opposed to electro-copper	1·115
	Electro-zinc opposed to amalgamated copper . . .	1·114

Zinc surrounded by dilute Sulphuric Acid.

Strength of acid.	Calculated electromotive force.	E.M.F. observed with electro-copper opposed to amalgamated zinc.
H_2SO_4, $358H_2O$ = sp. gr. 1·010	$1·113+x+y$	1·129
H_2SO_4, $67H_2O$ = „ 1·050	$1·124+x+y$	1·139
H_2SO_4, $37H_2O$ = „ 1·090	$1·128+x+y$	1·148
H_2SO_4, $17H_2O$ = „ 1·175	$1·141+x+y$	1·169

where y is a small quantity corresponding to the heat absorbed on dilution of the zinc sulphate to $ZnSO_4, 800H_2O$.

It is hence evident that in all cases the agreement between the E.M.F. actually developed and that due to the net chemical and physical actions taking place is so close, that what differences exist lie within the limits of experimental error; so that, finally, the conclusion may be drawn that, under favourable conditions, the E.M.F. of a Daniell cell is that due to the net resultant of the various physical and chemical actions taking place, the whole of the energy being adjuvant, viz. that gained by the displacement from copper-sulphate solution of copper by zinc, together with that gained by the transformation into ordinary electro-metal of the "nascent" copper first thrown down by the action; whilst under other conditions the E.M.F. falls below this amount, even after making allowance for the effect of the migration of the ions in causing solutions of different specific gravities to accumulate round the plates, indicating non-adjuvancy of one or other or both of these component portions of the total energy gained.

Experiments made with a view to find whether the Fall in E.M.F. on increasing the Current-density is mainly dependent on changes taking place in connexion with the actions at the surface of the Zinc or at that of the Copper plate.

115. In order to trace out somewhat more completely, if possible, how far that amount of fall in the E.M.F. of a Daniell cell taking place as the current generated increases, which is not due to the accumulation of solutions of zinc and copper of different densities round the plates, can be attributed to actions taking place at one or the other plate respectively,

the experiments described above (§103, 104) were repeated, with the difference that, instead of two sets of readings only being made (viz. when the two larger and the two smaller plates respectively were opposed), four sets were made—(1) when the two larger plates were opposed, (2) with the larger zinc and smaller copper, (3) with the two smaller plates, and (4) with the smaller zinc and larger copper plates opposed. By interpolation from the direct observational results, the differences of potential between the plates for any constant current-value were then calculated in each of the four cases. By comparing the values thus obtained in cases (1) and (2) and in (4) and (3), two sets of differences were obtained, indicating the effects produced by halving the area of the copper plate, every thing else being the same throughout, saving that with results (1) and (2) the larger zinc plate, and with the other pair of results the smaller zinc plate, was opposed to the two copper plates respectively: although this modified the actual values obtained in each of the original sets of readings, yet it produced practically no effect on the differences. In just the same way, by comparing the interpolation values in cases (1) and (4) and in (2) and (3), two corresponding sets of differences were obtained, indicating the effects produced by halving the area of the zinc plate; as before, the two sets substantially coincided. Various experiments of this kind were made with different plate-materials and fluids surrounding them: whilst the numerical values obtained were found to be to some extent variable with these conditions, yet, on the whole, it was always found that *the effect of halving the area of the copper plate notably exceeded that of halving the area of the zinc plate.* For instance, the following numbers were obtained in one set of observations with a cell containing bright pure zinc plates surrounded by zinc-sulphate solution of sp. gr. 1·42, and freshly-coated electro-copper plates surrounded by copper-sulphate solutions of sp. gr. 1·175, the larger plates exposing a surface of 5·0 square centimetres, and the smaller ones exposing 2·5 square centimetres.

	Effect of halving the area of the copper plate.						
Current, in micro-ampères.	Larger zinc plate opposed.			Smaller zinc plate opposed.			Mean difference.
	(1) Larger copper.	(2) Smaller copper.	Difference.	(4) Larger copper.	(3) Smaller copper.	Difference.	
100	1·082	1·078	·004	1·076	1·073	·003	·0035
200	1·071	1·066	·005	1·064	1·060	·004	·0045
500	1·061	1·055	·006	1·052	1·047	·005	·0055
1,000	1·045	1·036	·009	1·035	1·026	·009	·0090
2,000	1·026	1·015	·011	1·011	·999	·012	·0115
5,000	·964	·947	·017	·950	·929	·021	·0190
10,000	·876	·843	·033	·854	·820	·034	·0335
20,000	·729	·672	·057	·698	·639	·059	·0580

	Effect of halving the area of the zinc plate.						
Current, in micro-ampères.	Larger copper plate opposed.			Smaller copper plate opposed.			Mean difference.
	(1) Larger zinc.	(4) Smaller zinc.	Difference.	(2) Larger zinc.	(3) Smaller zinc.	Difference.	
100	1·082	1·076	·006	1·078	1·073	·005	·0055
200	1·071	1·064	·007	1·066	1·060	·006	·0065
500	1·061	1·052	·009	1·055	1·047	·008	·0085
1,000	1·045	1·035	·010	1·036	1·026	·010	·0100
2,000	1·026	1·011	·013	1·015	·999	·016	·0145
5,000	·964	·950	·014	·947	·929	·018	·0160
10,000	·876	·854	·022	·843	·820	·023	·0225
20,000	·729	·698	·031	·672	·639	·033	·0320

116. In precisely the same way, the ollowing mean difference-values were obtained in two other analogous experiments, in the first of which the zinc plates were amalgamated and immersed in zinc-sulphate solution sp. gr. 1·42, the copper plates being also amalgamated and immersed in copper-sulphate solution sp. gr. 1·175; and in the second of which electro-copper plates and copper-sulphate solution sp. gr. 1·175 were employed, conjoined with amalgamated zinc plates immersed in dilute sulphuric acid sp. gr. 1·045. The above mean difference-values are also exhibited in the table.

Current, in micro-ampères.	Amalgamated zinc and amalgamated copper—zinc sulphate solution. Effect of halving area of		Amalgamated zinc and electro-copper—dilute sulphuric acid. Effect of halving area of		Bright zinc and electro-copper—zinc-sulphate solution. Effect of halving area of	
	Copper.	Zinc.	Copper.	Zinc.	Copper.	Zinc.
100	·001	·001	·001	·001	·0035	·0055
200	·004	·002	·002	·003	·0045	·0065
500	·009	·003	·003	·005	·0055	·0085
1,000	·015	·004	·005	·007	·0090	·0100
2,000	·024	·005	·011	·010	·0115	·0145
5,000	·040	·009	·020	·015	·0190	·0160
10,000	·049	·017	·041	·020	·0335	·0225
20,000	·058	·026	·056	·032	·0580	·0320

Much the same kind of result was obtained in various other similar experiments; the effect of halving the area of the copper plate was, especially with the stronger currents, much more marked than that of halving the area of the zinc plate. The actual value of the depreciation produced with the stronger currents in either case, moreover, clearly indicates that the diminution cannot psssibly be solely due to the formation of stronger zinc-sulphate solution round the zinc plate, and weaker copper-sulphate round the copper plate, in the case of the smaller areas, than are produced with the larger ones; and hence the conclusion is arrived at that when, by reason of the production of a current, the E.M.F. of a Daniell cell is diminished, and the energy developed becomes proportionately non-adjuvant, the non-adjuvancy is ascribable, not merely to actions taking place at the surface of the zinc plate, but also, and more particularly, to those taking place at the surface of the copper plate. In the former case, the energy gained during the conversion of the metallic zinc of the plate into solution of zinc sulphate makes its appearance under such conditions partly as heat from the very commencement of the action, and is never wholly manifested as electric action expressible in volt-coulombs. In the latter case, the effect of the chemical action of the cell is to set free copper, which, in its transformation from the condition in which it is first set free (nascent copper) to the condition ultimately assumed (more or less compact electro-

deposited soft coherent metal), causes a gain of energy which, like that due to the solution of the zinc, is partly manifested as heat *ab origine*, and is never, under such conditions, obtained wholly as electric action. The actual proportion of the energy due to the solution of the zinc or to the agglomeration (or allotropic modification) of the copper which is thus non-adjuvant, is variable within certain limits with the conditions of the experiment, the nature of the plate-surfaces and of the liquids in the cell, &c., but, *cæteris paribus*, is greater the stronger the current: with very feeble currents (of density not exceeding some 8 microampères per square centimetre), the proportion of non-adjuvant energy is too small to be measurable.

Summary of Results.

117. The above-described experiments, and the conclusions to be drawn from them, may be thus summarized:—

1. When a Daniell cell is constructed with equal-sized plates of pure zinc and pure copper (either compact bright metals, amalgamated plates, or plates covered with electro-deposited metal) immersed respectively in solutions of pure zinc and copper sulphates of the same specific gravity, and is made to generate a current not exceeding in density some 8 microampères per square centimetre, an E.M.F. is set up varying within certain small limits according to the precise condition of the surfaces of the metals as regards polish, oxidation, &c., but always lying fairly close to 1·115 volt, and practically identical with the E.M.F. corresponding to the energy gained in the net chemical change ensuing, viz. the displacement of copper from copper-sulphate solution by zinc; so that under these conditions practically all the energy gained is adjuvant, whether due to displacement of copper by zinc, or to transformation into ordinary metal of the "nascent" copper thus set free.

2. When impure zinc, or pure zinc amalgamated with impure mercury, is used, a greater or less amount of the energy gained is non-adjuvant, even under conditions such as would with pure zinc cause all the energy to be adjuvant. The source of this non-adjuvancy evidently lies in the nature of the actions taking place at the surface of the zinc plate;

the maximum E.M.F. that such a cell can generate is more or less considerably below 1·115 volt, in some instances by several per cent.

3. When the density of the current exceeds 8 micro-ampères per square centimetre, the E.M.F. of the cell falls more or less below 1·115 volt, owing to three causes, each of which produces an effect in the direction of diminishing the E.M.F. First, according as the current density is greater or smaller, a greater or lesser degree of non-adjuvancy of the energy gained in the conversion of metallic zinc into zinc-sulphate solution is brought about. Secondly, a greater or lesser degree of non-adjuvancy is similarly brought about in the energy gained by the transformation into ordinary copper of the "nascent" metal liberated at the surface of the copper plate; other things being equal, this source of non-adjuvancy distinctly predominates over the other source just mentioned. Thirdly, the passage of the current causes a weaker solution of copper sulphate to be formed round the copper plate, and a stronger one of zinc sulphate to be produced round the zinc plate, than were originally used; this sets up an inverse E.M.F., and diminishes the effective E.M.F. of the cell. The maximum possible diminution due to this cause does not exceed ·04 volt; whilst with a current the density of which amounts to ·003 ampère per square centimetre and upwards, the total diminution due to this cause together with the non-adjuvancy amounts to several times this maximum possible value. The diminution due to these various causes jointly constitutes what is sometimes spoken of as the "polarization" of the cell.

4. When the solutions of zinc and copper sulphate employed are not of the same specific gravity, the E.M.F. of the combination differs from that which would have been set up had both been of the same specific gravity by an amount which increases with the difference in specific gravity of the two solutions: if the copper-sulphate solution is the stronger, the E.M.F. is increased, and *vice versâ*. The amounts of increase and decrease are sensibly the same as the electromotive forces generated when two copper-sulphate or two zinc-sulphate solutions interdiffuse, the specific gravities of which are identical respectively with those of the two fluids actually present in

the cell examined. So long as the two solutions are of the same specific gravity, the E.M.F. set up is, *cœteris paribus*, sensibly independent of the actual value of this specific gravity; at least the fluctuations observed are not outside the range of experimental errors.

5. When dilute sulphuric acid is used instead of zinc-sulphate solution, its specific gravity being the same as that of the copper-sulphate solution, an increase in the E.M.F. of the cell is produced which sensibly corresponds with the increase in the "heat of formation" of zinc sulphate when sulphuric acid is employed of the strength used in the cell, as compared with acid diluted to a larger extent (H_2SO_4, 800 H_2O). If the copper-sulphate solution differs from the acid in specific gravity, the latter not exceeding 1·18 in specific gravity, the E.M.F. is raised above or lowered below what it would have been had the copper sulphate been of the same specific gravity, by an amount which is sensibly the same as the E.M.F. generated by the interdiffusion of two copper-sulphate solutions the specific gravities of which are identical respectively with those of the two fluids actually present in the cell examined.

6. Owing to the diminution in the E.M.F. of a Daniell cell when generating a current, the fluctuations in the maximum values obtainable with any given cell with the physical condition of the surfaces of the plates and the time that has elapsed since its construction, the tendency to deposition of copper on the zinc by diffusion and the consequent diminution in E.M.F., and the variation in E.M.F. according as dilute acid of different strengths or zinc-sulphate solution is used to surround the zinc plate, it results that "the E.M.F. of a Daniell cell" is a very variable standard of E.M.F. and one singularly devoid of permanence. By taking suitable precautions in the construction of a cell (using pure zinc amalgamated with pure mercury, amalgamated or electro-copper, and pure zinc- and copper-sulphate solutions of the same specific gravity), a cell may be obtained the E.M.F. of which does not differ more than $\pm 0{\cdot}25$ per cent. from 1·113 or 1·114 volt, according as amalgamated or electro-copper is used; but such a cell cannot be kept many hours without altering in value materially, and is in practice a very far less

convenient standard than the mecurous-sulphate cell of Latimer Clark; for, notwithstanding that the limits of variation between two cells of this latter kind, similarly prepared, are somewhat greater than those of the best form of standard Daniell cell, it nevertheless possesses the valuable property of remaining sensibly constant (the temperature being the same) for many months, and even one or more years, as will be more completely shown in a future paper.

VIII. *On the Electric Resistance of Carbon under Pressure.* *By* Professor Silvanus P. Thompson, *B.A.*, *D.Sc.**

§ 1. It has often been stated that the electric resistance of carbon decreases when subjected (1) to an increase of temperature, (2) to a mechanical compression. The first of these statements has been verified by so many authorities that there can hardly be any question of its correctness. The second I believe to be wholly misleading; for some careful experiments that I have lately made lead to the conclusion that the effect of mechanical compression upon the electric resistance of dense carbon is almost, if not quite, *nil*, and that what has been mistaken for an increase in electric conductivity is in reality merely better contact at the points of junction with the circuit.

§ 2. A preliminary experiment to test whether the alleged decrease of resistance by pressure was due to a true increase in specific conductivity or to better end-contact, was made in the following manner:—A thin cylindrical rod of Carré's dense artificial carbon (such as is used in electric lamps) was taken, its length being 72 centimetres. At a point about one fourth of its length from the end a groove was filed round it, and around it was bound tightly the end of a clean thin copper wire. It was placed vertically upon a piece of copper in an upright frame, so that pressure could be applied longitudinally at the top; a flat piece of copper was placed upon the top of it and pressed lightly upon it. The point at which the thin wire was bound round it was then about 18 centim. from the lower end. The upper and lower portions were then

* Read February 25, 1882.

connected up with a Wheatstone's bridge, provided, as in Kirchhoff's pattern, with a wire of German silver stretched over a divided scale, the resistances of the two parts of the wire right and left being (when balance was obtained in the galvanometer) proportional respectively to the resistances of the two portions of the carbon rod. The relative, not the absolute, resistances of the two portions were therefore being measured. Two bichromate cells supplied the requisite current, the galvanometer being a short-coil astatic instrument of simple form.

On trying the resistances, it appeared that the resistance of the longer part, which was uppermost, was somewhat greater in respect to that of the lower and shorter part than would have been expected from their relative lengths; the ratio of their resistances being 81 : 19, or about 4·25 : 1, whereas their lengths were as 3 : 1 almost exactly. After taking the rod out of its place and putting it back again under light contact at the top as before, the ratio was found to be 82 : 18, or 4·55 : 1. The rod was thus removed and replaced several times; and the ratio of the resistances was found to differ somewhat every time, the figures varying from 4·7 : 1 to 3·92 : 1. Pressure was now applied at the top of the rod, and the ratio of the resistances was again measured. With a load of 5 kilogrammes (as much as it was judged the rod would bear without risking breaking it), the ratio of the resistances was found to be much more constant and much nearer to the ratio of the lengths of the two portions, being 75·3 : 24·7, which is not very different from 3 : 1. It was therefore clear that the previous values had been greatly affected by the differences in contact at the two ends; the lower contact having less resistance than the upper, in consequence of the superincumbent weight of the rod and connexions—about 19 grammes in total.

§ 3. Another rod of Carré's carbon was next examined, and its actual resistance measured in ohms. Its length was 42·6 centim., its diameter 0·48 centim. To prepare it for the experiment, it was electroplated with a thin coating of copper to the length of about 1 centim. at each end, the extremities being afterwards scraped bare of copper so that end-contacts should be made against the carbon itself. Copper wires were then carefully soldered to the copper coating at about 0·5

centim. from the ends. The object of this arrangement was to render possible a comparison between the resistance of the rod when there was merely end-contact—which might be more or less perfect according to the pressure—and the resistance of the rod as measured when there was a perfect contact through the deposited coatings of copper. The rod was then laid in a horizontal frame, where it reposed on two Y-shaped bearings—one end pressing against a lever-arrangement for the purpose of putting on a measurable amount of pressure, the rod being fixed at the other end by abutting against a brass set-screw. A copper piece was introduced between the lever and the extremity of the rod, in order to provide an end-contact; and arrangements were made whereby the rod could be connected up in a Wheatstone-bridge, the connexion being made at pleasure either through the end-contacts or through the copper-plated junctions.

The resistance of the rod between the copper-plated junctions was then measured, the rod being free at both ends. It was found to be $0{\cdot}56 \pm 0{\cdot}007$ ohm. The end-contacts were then made to touch lightly (the circuit through them remaining open). The resistance through the copper-plated junctions showed no change. Pressure was then applied to the rod longitudinally, and augmented until it began to show lateral distortion, the effective force along the rod being 4150 grms., equivalent (if the area of cross section of the rod be taken as 0·18 square centim.) to 23,055 grms. per square centimetre. Yet, even under this pressure, not the smallest change could be detected in the resistance between the copper-plated junctions. If there was any, it was certainly less than 0·005 ohm, or less than 1 per cent. of the whole resistance.

The circuit was now made through the end-contacts by moving the set-screw until the lightest possible contact was obtained, the connexions through the copper-plated junctions having been thrown out of circuit. The resistance thus determined was 1·1 ohm. Pressure was applied as before. The resistance fell to 0·72 ohm when the pressure of 23 kilogrammes per square centimetre was reached. On releasing the pressure, the resistance again rose until contact became as light as possible. The resistance attained 1·08 ohm, when it rose abruptly to infinity as the set-screw ceased to touch the

end of the rod. The battery and galvanometer used throughout were the same as described above.

Nothing could be more significant than these observations. When perfect contact was ensured by electroplating, pressure produced no effect on the resistance of the carbon rod, or one inappreciably small. When circuit was made by pressing pieces of copper and brass against the rough ends of the carbon rod, contact was only imperfectly obtained, and the resistance varied with the pressure because increased pressure brought about better contact, or contact at a greater number of points.

The bearing of these observations upon the theory of the carbon rheostat, the carbon relay, the carbon transmitting-telephone, and the carbon microphone is obvious.

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